ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

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CONTENTS.

TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	FULL TITLE.
A.	Abstracts in Journal of the Chemical Society (until 1925) or in British Chemical Abstracts,* Section A.
Acta Phytochim. . . .	Acta Phytochimica.
Amer. Inst. Met. Eng. Tech. Pub.	American Institute of Mining and Metallurgical Engineers Technical Publications.
Amer. J. Bot. . . .	American Journal of Botany.
Amer. J. Pharm. . . .	American Journal of Pharmacy.
Amer. J. Sci. . . .	American Journal of Science.
Amer. Min.	American Mineralogist.
Anal. Asoc. Quím. Argentina	Anales de la Asociación Química Argentina.
Anal. Farm. Bioquím. .	Anales de Farmacia y Bioquímica (Buenos Aires).
Anal. Fís. Quím. . . .	Anales de la Sociedad Espanõla Física y Química.
Analyst	The Analyst.
Angew. Bot.	Angewandte Botanik.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Acad. Brasil. Sci. .	Annals da Academia Brasileira de Sciencias.
Ann. Bot.	Annals of Botany.
Ann. Chim.	Annales de Chimie.
Ann. Chim. analyt. . .	Annales de Chimie analytique et de Chimie appliquée.
Ann. Chim. Appl. . .	Annali di Chimica Applicata.
Ann. Falsif.	Annales des Falsifications et des Fraudes.
Ann. Inst. Anal. Phys. Chem.	Annales de l'Institut d'Analyse physico-chimique, Leningrad.
Ann. Physik . . .	Annalen der Physik.
Ann. Reports . . .	Annual Reports of the Chemical Society.
Ann. Sci. agron. franç. .	Annales de la Science agronomique française et etrangère.
Ann. Soc. Sci. Bruxelles .	Annales et Bulletin de la Société royale des Sciences médicales et naturelles de Bruxelles.
Apoth.-Ztg.	Apotheker-Zeitung.
Arch. Eisenhüttenw. . .	Archiv für das Eisenhüttenwesen.
Arch. Pharm. . . .	Archiv der Pharmazie.
Arch. Physique biol. . .	Archives de Physique biologique.
Arch. Sci. phys. nat. . .	Archives des Sciences physiques et naturelles.
Arhiv Hemiju . . .	Arhiv za Hemiju i Farmaciju.
Arizona Agric. Exp. Sta. Tech. Bull.	Arizona Agricultural Experimental Stations Technical Bulletins.
Arkiv Kemi, Min. Geol. .	Arkiv för Kemi, Mineralogi och Geologi.
Atti III Cong. Naz. Chim.	Atti del III° Congresso nazionale di Chimica pura ed applicata (May, 1929).
Atti R. Accad. Lincei . .	Atti (Rendiconti, Memorie) della Reale Accademia Nazionale dei Lincei, classe di scienze fisiche, matematiche e naturali, Roma.
Atti R. Accad. Sci. Torino .	Atti della Reale Accademia delle Scienze di Torino.
Australian J. Exp. Biol. Med. Sci.	The Australian Journal of Experimental Biology and Medical Science.
B.	British Chemical Abstracts,* Section B.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Ber. deut. bot. Ges. . .	Berichte der deutschen botanischen Gesellschaft.
Ber. deut. physikal. Ges. .	Berichte der deutschen physikalischen Gesellschaft.
Biochem. J.	The Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Boll. chim.-farm. . . .	Bolletino chimico-farmaceutico.
Bot. Gaz.	The Botanical Gazette.
Brennstoff.-Chem. . .	Brennstoff-Chemie.
Brit. J. Exper. Path. . .	The British Journal of Experimental Pathology.

* The year is not inserted in references to 1931

Abbreviated Title.	FULL TITLE.
Bul. Chim. Soc. Română Stiin.	Buletinul de Chimie pură si applicată Societatea Română de Stiinte.
Bul. Soc. Stiinte Cluj	Buletinul Societătii de Stiinte din Cluj.
Bull. Acad. Polonaise	Bulletin Internationale de l'Académie Polonaise des Sciences et des Lettres.
Bull. Acad. roy. Belg.	Académie royale de Belgique.—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientifique de l'Académie Roumaine.
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie et des Industries Agricoles de France et des Colonies.
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan.
Bull. Sci. pharmacol.	Bulletin des Sciences pharmacologiques.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chimie biologique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. Pharm. Bordeaux	Bulletin des Travaux de la Société de Pharmacie de Bordeaux.
Bull. Torrey Bot. Club	Bulletin of the Torrey Botanical Club.
Bull. Trav. Dep. Chim. Inst. Hyg. État.	Bulletin des Travaux du Département de Chimie de l'Institut d'Hygiène d'État (Warsaw).
Bull. Univ. Asie centrale	Bulletin de l'Université de l'Asie centrale.
Bull. West Va. Univ. Sci. Assoc.	Bulletin of the West Virginia University Scientific Association.
Bur. Stand. J. Res.	Bureau of Standards Journal of Research.
Canadian J. Res.	Canadian Journal of Research.
Cellulosechem.	Cellulosechemie. Zeitschrift für Gerüst-, Inkrustations- und andere Begleitstoffe der Cellulose.
Centr. Min.	Centralblatt für Mineralogie, Geologie, und Paläontologie.
Chem. and Ind.	Chemistry and Industry.
Chem. Erde	Chemie der Erde.
Chem. Fabr.	Die Chemische Fabrik.
Chem. Listy	Chemické Listy pro Vědu a Průmysl. Organ de la "Ceská chemická Společnost pro Vědu a Průmysl."
Chem. News	Chemical News.
Chem. Obzor	Chemický Obzor.
Chem. Reviews	Chemical Reviews.
Chem. Umschau	Chemische Umschau auf dem Gebiete der Fette, Oele, Wachse, und Harze.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zentr.	Chemisches Zentralblatt.
Chem.-Ztg.	Chemiker-Zeitung.
Coll. Czech. Chem. Comm.	Collection of Czechoslovak Chemical Communications.
Coll. Symp. Ann.	Colloid Symposium Annual.
Coll. Symp. Monograph	Colloid Symposium Monograph (now issued under foregoing title).
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biology.
Contr. Boyce Thompson Inst.	Contributions from Boyce Thompson Institute.
Dansk Tidsskr. Farm.	Dansk Tidsskrift for Farmaci.
Deut. Z. gerichtl. Med.	Deutsche Zeitschrift für die gesammte gerichtliche Medizin.
Ergeb. Agrik.-chem.	Ergebnisse der Agrikulturchemie.
Farm. Zhur.	Farmatzevtichnii Zhurnal.

Abbreviated Title.	FULL TITLE.
Förh. III Nord. Kemistmötet	Nordiska Kemistmötet Förhandlingar och Föredrag, 3rd Meeting, Helsingfors.
Fortschr. Min.	Fortschritte der Mineralogie, Kristallographie und Petrographie.
Gazzetta	Gazzetta chimica italiana.
Helv. Chim. Acta	Helvetica Chimica Acta.
Illinois Agric. Exp. Sta. Tech. Bull.	Illinois Agricultural Experimental Stations Technical Bulletins.
Ind. Chem.	The Industrial Chemist and Chemical Manufacturer.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
Ind. Eng. Chem. (Anal.)	Industrial and Engineering Chemistry: Analytical Edition.
Indian J. Physics	Indian Journal of Physics.
Iowa State Coll. J. Sci.	Iowa State College Journal of Science.
J.	Journal of the Chemical Society.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	The Journal of Agricultural Science.
J. Amer. Ceramic Soc.	Journal of the American Ceramic Society.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.
J. Amer. Soc. Agron.	Journal of the American Society of Agronomy.
J. Appl. Chem. Russia	Zhurnal prikladnoi Chimii.
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
J. Biochem. Japan	Journal of Biochemistry (Japan).
J. Biol. Chem.	Journal of Biological Chemistry.
J. Chem. Ind. Russia	Journal of Chemical Industry of Russia.
J. Chim. physique	Journal de Chimie physique.
J. Counc. Sci. Ind. Res. Australia	Journal of the Council for Scientific and Industrial Research (Australia).
J. Dept. Agric. S. Australia	Journal of the Department of Agriculture of South Australia.
J. Econ. Entom.	Journal of Economic Entomology.
J. Exp. Agron. Russia	Journal of Experimental Agronomy, Russia.
J. Exp. Med.	Journal of Experimental Medicine.
J. Fac. Agric. Hokkaido	Journal of the Faculty of Agriculture, Hokkaido Imperial University.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Chem. Russia	Journal of General Chemistry (Russia).
J. Gen. Physiol.	Journal of General Physiology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry (now Industrial and Engineering Chemistry).
J. Indian Chem. Soc.	Quarterly Journal of the Indian Chemical Society.
J. Indian Inst. Sci.	Journal of the Indian Institute of Science.
J. Inst. Metals	Journal of the Institute of Metals.
J. Iron Steel Inst.	Journal of the Iron and Steel Institute.
J. Landw.	Journal für Landwirtschaft.
J. Pharm. Belg.	Journal de Pharmacie de Belgique.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan (Yakugakuzasshi).
J. Phys. Radium	Journal de Physique et le Radium.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	The Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Sci. Inst.	Journal of Scientific Instruments.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Chem. Ind. Japan	Journal of the Society of Chemical Industry, Japan (Kōgyō Kwagaku Zasshi).
J. Soc. Dyers Col.	Journal of the Society of Dyers and Colourists.

Abbreviated Title.	FULL TITLE.
J. Soc. Glass. Tech. . .	Journal of the Society of Glass Technology.
J. Soc. Leather Trades' Chem.	Journal of the International Society of Leather Trades' Chemists.
J. Text. Inst. . . .	The Journal of the Textile Institute.
J. Text. Sci.	Journal of Textile Science.
Jahrb. kgl. preuss. geolog. Landesanst. Bergakad.	Jahrbuch der königlichen preussischen geologischen Landesanstalt und Bergakademie.
Jahrb. Min., Beil.-Bd. .	Neues Jahrbuch für Mineralogie, Geologie und Paläontologie, Beilage-Band.
Jahrb. wiss. Bot. . . .	Jahrbücher für wissenschaftliche Botanik.
K. Svenska Vetenskaps Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar.
Kolloidchem. Beih. . .	Kolloidchemische Beihefte.
Kolloid-Z.	Kolloid-Zeitschrift.
Lancet	The Lancet.
Landbouw. (*Java*) . .	Landbouwkundige Serie (Proefstation voor de Java Suikerindustrie).
Landw. Jahrb. . . .	Landwirtschaftliche Jahrbücher.
Latvij. Univ. Raksti . .	Latvijas Universitātes Raksti.
Magyar Chem. Fol. . .	Magyar Chemiai Folyóirat (Hungarian Chemical Journal).
Magyar Gyó. Társas. Ért. .	Magyar Gyógyszerésztudományi Társaság Értesitöje.
Mem. Coll. Sci. Kyoto .	Memoirs of the College of Science, Kyoto Imperial University.
Mem. Dept. Agric. India .	Memoirs of the Department of Agriculture in India.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mém. Poudres . . .	Mémorial des Poudres.
Mem. Ryojun Coll. Eng. .	Memoirs of the Ryojun College of Engineering.
Met. and Alloys . . .	Metals and Alloys.
Metal Ind.	The Metal Industry (London).
Metall u. Erz . . .	Metall und Erz.
Metallwirt.	Metallwirtschaft, Metallwissenschaft, Metalltechnik.
Mikrochem.	Mikrochemie.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Missouri Exp. Sta. Res. Bull.	Missouri Experimental Stations Research Bulletins.
Mitt. deut. Material-prüf. Berlin-Dahlem	Mitteilungen der deutschen Materialprüfungsanstalten.
Mitt. Kaiser-Wilh. Inst. Eisenforsch.	Mitteilungen aus dem Kaiser-Wilhelm Institut für Eisenforschung zu Düsseldorf.
Mitt. kgl. bayr. Moorkulturanstalt	Mitteilungen der königlichen baeyerischen Moorkulturanstalt.
Mitt. Lebensm. Hyg. . .	Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
N. Carolina Agric. Exp. Sta. Tech. Bull.	North Carolina Agricultural Experimental Stations Technical Bulletins.
Nach. Ges. Wiss. Göttingen.	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Nat. Centr. Univ. Sci. Rep.	National Central University (Nanking) Science Reports.
Naturwiss.	Die Naturwissenschaften.
Natuurwetensch. Tijds. .	Natuurwetenschappelijk Tijdschrift.
Neft. Khoz.	Neftyanoe Khozyaĭstvo (Petroleum Industry).
New Hamps. Agric. Exp. Sta. Bull.	New Hampshire Agricultural Experimental Stations Bulletins.
Nippon Kogyokwaishi .	Nippon Kwagaku Kwaishi (Journal of the Chemical Society of Japan).
Norsk Geol. Tidsskr. . .	Norsk Geologisk Tidsskrift.

Abbreviated Title.	FULL TITLE.
Norsk Videnskabsselskab.	Skrifter udg. af Videnskabsselskabet i Oslo.
Nova Acta (Upsala)	Nova Acta Regiae Societatis Scientiarum Upsaliensis.
Nuovo Cim.	Il Nuovo Cimento.
Oesterr. bot. Z.	Oesterreichische botanische Zeitschrift.
Oesterr. Chem.-Ztg.	Oesterreichische Chemiker-Zeitung.
Ohio Agric. Exp. Sta. Bull.	Ohio Agricultural Experimental Station Bulletins.
Pflanzenbau	Wissenschaftliches Archiv für Landwirtschaft. Abteilung A. Pflanzenbau.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zentr.	Pharmazeutische Zentralhalle.
Pharm.-Ztg.	Pharmazeutische Zeitung.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phot. J.	The Photographical Journal.
Physical Rev.	Physical Review.
Physikal. Z.	Physikalische Zeitschrift.
Phytopath.	Phytopathology.
Plant Physiol.	Plant Physiology.
Planta	Zeitschrift für wissenschaftliche Biologie. Abteilung E. Planta. Archiv für wissenschaftliche Botanik.
Poln. Jahrb. Land- u. Forstwirts.	Polish Agricultural and Forestal Annual.
Proc. Acad. Sci. Amsterdam	Proceedings of the Royal Academy of Sciences of Amsterdam (English Version).
Proc. Amer. Acad.	Proceedings of the American Academy of Arts and Sciences.
Proc. Assoc. Southern Agric. Workers	Proceedings of the Association of Southern Agricultural Workers.
Proc. Imp. Acad. Tokyo	Proceedings of the Imperial Academy of Japan.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam.
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Nova Scotian Inst. Sci.	Proceedings of the Nova Scotian Institute of Science.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Protoplasma	Internationale Zeitschrift für physikalische Chemie des Protoplasten.
Przemysł Chem.	Przemysł Chemiczny.
Quart. J. Pharm.	Quarterly Journal of Pharmacy and Pharmacology.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rev. brasil. Chim.	Revista brasileira de Chimica.
Rev. Chim. pura appl.	Revista de Chimica pura e applicata.
Rev. Fac. Cienc. quím. La Plata	Revista de la Facultad de Ciencias químicas (Universidad nacional de La Plata).
Rev. gén. Colloïd.	Revue générale des Colloïdes.
Rhode I. Agric. Exp. Sta. Bull.	Rhode Island Agricultural Experimental Stations Bulletins.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Schweiz. med. Woch.	Schweizerische medizinische Wochenschrift.
Sci. Papers Inst. Phys. Chem. Res. Tokyo	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Rep. Tôhoku Imp. Univ.	Scientific Reports, Tôhoku Imperial University.
Semana méd.	La Semana médica (Buenos Aires).

Abbreviated Title.	FULL TITLE.
Sitzungsber. Heidelberger Akad. Wiss.	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Soil Sci.	Soil Science.
Sprechsaal	Sprechsaal für Keramik, Glas und verwandte Industrien Fach- und Wirtschaftsblatt.
Stahl u. Eisen . . .	Stahl und Eisen.
State Inst. Tobacco Invest. Bull. (*U.S.S.R.*)	State Institute for Tobacco Investigations.
Suomen Kem. . . .	Suomen Kemistilehte (Acta Chemica Fennica).
Svensk Kem. Tidskr. . .	Svensk Kemisk Tidskrift.
Tech. Rep. Tôhoku . .	The Technology Reports of the Tôhoku Imperial University.
Tidsskr. Kjemi Berg. . .	Tidsskrift for Kjemi og Bergvaesen.
Trans. Ceramic Soc. . .	Transactions of the Ceramic Society.
Trans. Faraday Soc. . .	Transactions of the Faraday Society.
Trans. Inst. Pure Chem. Reag.	Transactions of the Institute of Pure Chemical Reagents (Moscow).
Trans. Roy. Soc. Canada .	Transactions of the Royal Society of Canada.
Trans. Sci. Inst. Fert. .	Transactions of the Scientific Institute of Fertilisers (Moscow).
Trans. State Inst. Test. Building Mat. . . .	Transactions of the State Institute for Testing Building Materials and Glass.
Tsch. min. petr. Mitt. .	Tschermaks mineralogische und petrographische Mitteilungen.
Tzvet. Met.	Tzvetnine Metallni (Non-ferrous Metals).
Udobr. Urozhai . . .	Udobrenie i Urozhai (Fertilisers and Crops).
Ukraine Chem. J. . .	Ukraine Chemical Journal.
U.S. Dept. of Agric. . .	United States Department of Agriculture.
U.S. Public Health Rep. .	United States Public Health Service : Public Health Reports.
Univ. of Calif. Expt. Sta. of Coll. of Agric.	University of California, Experimental Station of the College of Agriculture.
Univ. Toronto Studies Geology	University of Toronto Studies : Geological Series.
Verhandl. II Komm. Intern. Bodenkunde Gesell. Budapest	International Society of Soil Science (German Version of Proceedings at 2nd Meeting).
Welsh J. Agric. . . .	The Welsh Journal of Agriculture.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. angew Chem.	Zeitschrift für angewandte Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Elektrochem.	Zeitschrift für Elektrochemie (und angewandte physikalische Chemie).
Z. Krist.	Zeitschrift für Kristallographie.
Z. Metallk.	Zeitschrift für Metallkunde.
Z. Parasitenk.	Zeitschrift für Parasitenkunde (Abteilung F. Zeitschrift für wissenschaftliche Biologie).
Z. Pflanz. Düng. . . .	Zeitschrift für Pflanzenernährung und Düngung.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem. . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physiol. Chem. . . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. tech. Physik. . . .	Zeitschrift für technische Physik.
Z. Unters. Lebensm. . .	Zeitschrift für Untersuchung der Lebensmittel.
Z. wiss. Mikr.	Zeitschrift für wissenschaftliche Mikroskopie und für mikroskopische Technik.
Z. wiss. Phot.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Zement	Zement (Wochenschrift für Hoch- und Tiefbau).

ANNUAL REPORTS

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PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

MUCH of the work published during the past year has been devoted to extending or consolidating advances to which reference has already been made in these Reports. This circumstance has not rendered any easier than usual the selection of matters to be discussed. The following pages, therefore, can in no sense claim to be complete : at best it may be hoped that they will provide a more or less representative sample of the kind of investigation which has been going on. In the newer quantum theory no fundamental advances have been made, but there have been several important applications to problems of chemistry. The interest of these applications is so great that the possibility of simplifying the mathematical technique of quantum mechanics, even with some sacrifice of formal accuracy, is one which should be very well worth exploring.

Definite advances are being made in solving the problem of the structure of the atomic nucleus, but so far there is not even the glimmering of a theory about the forces which hold the nucleus together.

There has been much valuable systematic work in connexion with the theory of solutions, crystal structure, and especially the elucidation of molecular structure with the aid of measurements of dipole moments and of the Raman effect. In the field of chemical kinetics there has also been considerable activity.

Atoms, Electrons, and Protons.

Much work has been published dealing with the theoretical implications of the quantum mechanics. The success of this in giving a quantitative account of a very large variety of physical phenomena is more and more demonstrated : but the feeling is also growing that something more fundamental than the formalism of this calculus is desirable, and that there may, for example, be something to be said for re-introducing phase relationships in dealing

with atomic interactions,[1] instead of treating the matter entirely in terms of the rather difficultly understandable exchange energy. But the time is hardly ripe for the discussion of this in these Reports.

There have been several more detailed discussions of the theory of molecular forces,[2] including interesting attempts to draw conclusions about molecular structure (see following section).[3] Another development of interest to chemists is the discussion from the quantum mechanical point of view of collision processes and the conditions governing the interchange of energy which may occur during them. C. Zener,[4] for example, considers the collision between an atom and a diatomic molecule : it appears that in simple systems the probability of an interchange of vibrational energy is quite a small one. Ionic and electronic collisions have also been considered by a number of authors. The variation of effective atomic cross section for various types of electronic collision is discussed by H. S. W. Massey and C. B. O. Mohr.[5] In a general way it appears that the complex experimental relationships can be accounted for.

Experimental work on the diffraction of electrons has continued.[6] P. M. S. Blackett and F. C. Champion [7] have studied the scattering of slow α-particles by helium and confirmed Mott's theory of the process, which yields results differing from classical theory.

The most interesting development in the whole field is probably the experimental one due to Rutherford and his school, which carries us a step further in the understanding of the nature of the atomic nucleus. For the last year or two interest has been rather centred on the quantum mechanical theory of nuclear disintegration, which gives in general terms a roughly quantitative description of the phenomena of α-particle emission, but, from its nature, does not tell much about the structure of the nucleus or the " mechanism " of disintegration. The success of the new investigation depends upon a method for counting α-particles accurately: [8] the small ionisation current caused by the particle traversing a few millimetres of its

[1] Compare R. M. Langer, Buffalo Meeting of Amer. Chem. Soc., Sept. 1931.

[2] W. Heitler and G. Rumer, *Z. Physik*, 1931, **68**, 12; *A.*, 547; R. de L. Kronig and W. G. Penney, *Proc. Roy. Soc.*, 1931, [*A*], **130**, 499; *A.*, 407; M. Delbrück, *ibid.*, 1930, [*A*], **129**, 686; *A.*, 17; J. E. Lennard-Jones, *ibid.*, p. 598; *A.*, 17; F. Hund, *Z. Physik*, 1931, **73**, 1.

[3] L. Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367; *A.*, 670.

[4] *Physical Rev.*, 1931, **37**, 556; *A.*, 543.

[5] *Proc. Roy. Soc.*, 1931, [*A*], **132**, 605.

[6] F. L. Arnot, *ibid.*, 1931, [*A*], **130**, 655; *A.*, 542; R. Wierl, *Ann. Physik*, 1931, **8**, 521; *A.*, 665.

[7] *Proc. Roy. Soc.*, 1931, [*A*], **130**, 380; *A.*, 280.

[8] (Sir) E. Rutherford, F. A. B. Ward, and C. E. Wynn-Williams, *ibid.*, 1930, [*A*], **129**, 211; *A.*, 1930, 1338; C. E. Wynn-Williams and F. A. B. Ward, *ibid.*, 1931, [*A*], **131**, 391; *A.*, 666.

path is amplified by means of a valve. The corresponding ionisation produced by a β-particle is too small to be recorded. By suitable arrangement of the amplifying and recording system it is possible to count α-particles even in presence of a strong γ-radiation. A differential method was then developed which allowed the counting of those particles having ranges between say x and x plus a few millimetres, instead of as usual the total number with ranges exceeding a given amount. This was rendered possible by the use of a double ionisation chamber of special construction : the number stopping within a region about 2 mm. broad could be detected and counted. With the new counter it was possible to detect the missing short-range α-particles from the dual disintegration of radium-*C*—those corresponding to the *C''* branch.

Since 1919 it has been known that radium-*C*, in addition to the normal 7-cm. range particles, gave rise to a group of long-range particles. Analysis of these by the new method reveals [9] the fact that they can be resolved into at least 9 homogeneous groups between 7 cm. and 12 cm. range, the ranges and relative numbers in each group being determined. From the ranges the velocities and energies can be estimated by the usual methods. The existence of these long-range groups is now correlated with the emission of γ-rays in a remarkable manner.

The general theoretical picture is as follows. Radium-*C* emits a β-particle giving rise to radium-*C'* : some of the α-particles in the new nucleus are in excited levels, from which they either escape as long-range particles, or fall to a lower level with emission of a γ-ray. It is from the ground level of the radium-*C'* nucleus that the normal 7-cm. range particles are supposed to come. (In certain cases there may be emitted instead of the γ-ray itself a β-particle liberated from the outer atom by some process of internal conversion.)[10] The first point which emerges is that the maximum energy which could be released in a transition from a level corresponding to the particles of highest energy to the ground level is about equal to the maximum energy of any β-ray line in the magnetic spectrum of radium-*C* (these lines come largely from the conversion of γ-rays).

From the energies of the fast α-particles a series of energy levels above the normal level can be calculated. Assumed transitions between these or from them to the ground level can then be compared with the energies of γ-rays or the corresponding β-rays of the magnetic spectrum. The intensity of the γ-rays is of the order of one quantum

[9] (Lord) Rutherford, F. A. B. Ward, and W. B. Lewis, *Proc. Roy. Soc.*, 1931, [*A*], **131**, 684; *A.*, 890.

[10] Compare R. H. Fowler, *ibid.*, 1930, [*A*], **129**, 1; *A.*, 1930, 1338; C. D. Ellis and G. H. Aston, *ibid.*, p. 180; *A.*, 1930, 1339.

for each two or three disintegrations, but the number of nuclei which disintegrate to give the fast particles is of the order of 1—10 in a million, so that the probability of a change in energy level with emission of radiation is very much greater than that of the escape of one of the "excited" α-particles. The energy differences of the α-particle states are not only of the same order of magnitude as the γ-ray energies, but in several examples numerical agreement was found, lending still stronger support to the idea that the quantum of γ-radiation is emitted during an α-particle transition in an excited nucleus.

Working on this basis, Lord Rutherford and C. D. Ellis [11] analyse the numerous γ-rays from radium-C' into an orderly scheme. Two kinds of energy-level system are theoretically possible. In the first, a given particle could occupy a series of energy levels of different quantum numbers, in a manner analogous to the successive electronic states of the hydrogen atom. In the second, the different levels are due to the excitation of varying numbers of particles to the same higher state. The Pauli principle rules out this second class of system for electronic states, but permits it in the case of α-particles. Rutherford and Ellis take as their working hypothesis the simple assumption that transitions occur whereby the number of particles in a single excited state changes in one act from r to r' with emission of a quantum of radiation. If ε_1 and ε_2 are the energies of each of the particles in the ground state and the excited state before the transition, and ε_1' and ε_2' the corresponding quantities after the transition, then, if n is the total number of particles, the total energies before and after the transition are given respectively by $(n - r)\varepsilon_1 + r\varepsilon_2$ and by $(n - r')\varepsilon_1' + r'\varepsilon_2'$ (ε_1' and ε_2' are changed because there is necessarily a mutual action of the α-particles). These considerations indicate that the energies of the γ-rays should be representable in the form $h\nu = pE_1 - qE_2$, where p and q are integers. The experimental data are found to be compatible with such a scheme, though it is not excluded that slightly different schemes might fit the facts equally well.

R. H. Fowler,[12] considering the quantum mechanical aspect of the problem in the light of these new results, finds by the analysis of a very rough and ready model, *viz.*, a one-dimensional model in which α-particles act on one another with potential energies of a quadratic form, that the energy levels are such as to give rise to γ-rays of frequencies represented by an expression of the form $h\nu = p(E_0 - qE_1)$. The necessary modification of the formula of Rutherford and Ellis would not do violence to the experimental facts.

[11] Compare R. H. Fowler, *Proc. Roy. Soc.*, 1931, [*A*], **132**, 667.
[12] *Nature*, 1931, **128**, 453.

Physical Theory and Benzene Structure.

In the last Report reference was made to the work of E. Hückel on the quantum mechanical interpretation of the " rigidity " of chemical double bonds. The simpler structural problems of organic chemistry are so beautifully and completely treated with the aid of the traditional ideas that the translation of these ideas into the language of wave mechanics must be regarded rather as a satisfaction to the physicist than as a real advance in chemistry. But there are certain problems which the ordinary conceptions of chemistry have not been able to solve without the aid of auxiliary ideas sometimes of a rather indefinite character. Prominent among these problems are the questions of the structure of aromatic compounds and the orientation of substituents in the benzene nucleus. Here especially the introduction of new guiding principles is particularly valuable, and we may well look with interest to see whether a quantum mechanical treatment does indeed go a step beyond re-interpreting well-tried old ones. It must be remarked at the outset that anything like a complete quantum mechanical analysis, starting from first principles, of a problem so complex as the structure of benzene is impossible. Even the treatment of the hydrogen molecule has to be based upon approximations, which already take for granted certain empirically established facts. For example, as F. Hund points out,[13] when Heitler and London neglected the Coulomb forces between two hydrogen atoms in comparison with the " exchange force " they were virtually taking advantage of the empirical information that the inert gases have in fact no chemical affinity. In dealing with benzene, therefore, Hückel [14] has to begin by making various assumptions the validity of which cannot be estimated except by reference to the results. Nevertheless, certain discoveries emerge which appear to be of great importance.

The method of analysis is based upon the fact that in benzene there are six bonds over and above those engaged in the single linkages of carbon to carbon or carbon to hydrogen. Thus there are six electrons not accommodated in ordinary non-polar single bonds (each carbon brings four outer electrons, each hydrogen one: total 30. The 12 single bonds require 24, leaving 6). Hückel takes the more general case of n CH groups in a ring and n electrons, and tries two methods of approximation. In the first, each electron is thought of as assigned to one ring atom in a definite quantum state, and the interaction between them is investigated by methods analogous to those which have been successfully applied to the determination of interaction in many-electron systems in connexion with ferromagnetic phenomena. It transpires that rings with an odd number

[13] *Z. Physik*, 1931, **73**, 1. [14] *Ibid.*, 1931, **70**, 204.

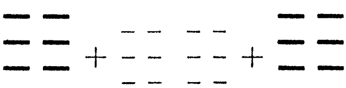
of carbon atoms should possess a greater energy content than those with an even number, but there appears to be no other result of obvious chemical interest. The second method of approximation neglects at first the "exchange energies" of the electrons, and considers the n electrons in a field of force which varies periodically round the ring. The possible quantum states of these electrons are worked out, and the important result appears that, when the Pauli principle is introduced (*i.e.*, that only two electrons of opposite spins can occupy the same quantum state), systems of electrons of 2, $2 + 4 = 6$, $2 + 4 + 4 = 10$ are found to constitute "closed groups," somewhat analogous to the closed groups in the atoms of the periodic system. Since C_2H_2 is not a ring and $C_{10}H_{10}$ is not known at all, the six-electron system occupies a unique place, and the stability of the closed group is evidently responsible for some of the characteristic properties of benzene and the aromatic compounds. The 8-group is not a closed one, which may well explain the well-known lack of aromatic character shown by *cyclo*octatetraene. Heterocyclic six-membered rings such as pyridine, or five-membered rings such as thiophen, in which the heterocyclic atom can contribute more than one electron can also show aromatic properties. Although the effect of the disturbed cyclic symmetry on the behaviour of the electrons in these examples cannot be calculated, it is not at all unreasonable to suppose that the importance of the closed groups of six persists. To sum up, we may say that while quantum mechanics cannot solve the benzene problem in anything like a complete way, it shows that there is good ground for believing that ring systems in which a group of six electrons unaccommodated in single bonds occurs will possess special properties and probably unusual stability. This appears to be a result of great importance.

Hückel has also dealt with the problem of benzene substitution,[15] making approximate estimates of the disturbance of charge distribution of the electrons caused by the presence of a substituent. According to his arguments, the negative charge in, for example, nitrobenzene is increased relative to benzene in the ortho- and para-positions and reduced in the meta-position, *i.e.*, in this example the electrons are " repelled from the carbon atom where the substitution has taken place and from the meta-carbon atom towards the ortho- and para-atoms." This is an effect of the opposite sign from that postulated by the simple theory of " alternating polarities," but according to Hückel a carbon atom where there is a defect of negative charge will repel a hydrogen nucleus, thereby lessening the work which must be done in removing it. Substitution thus becomes easier. Meta-substitution occurs therefore in the nitrobenzene example.

[15] *Z. Physik*, 1931, **72**, 310.

It should be mentioned in this connexion that L. E. Sutton [16] has shown by direct comparison of the dipole moments of corresponding aromatic and aliphatic compounds that " electron drifts " away from or towards the substituent group can in fact be detected. This is important, since for the first time it establishes the physical reality of the electrical changes which various current theories of organic reactions postulate.

The conception of the " electronic cloud " which Schrödinger's theory introduces has hitherto proved useful in forming a picture of several phenomena : *e.g.*, the interaction of the clouds was used by Hückel in interpreting the properties of the double bond, and his theory of induced polarities deals with disturbances of the electric density associated with the 6 " ring " electrons of benzene. In a still simpler example repelling or attracting hydrogen atoms with the aid of an unequal density distribution can be pictured thus :—



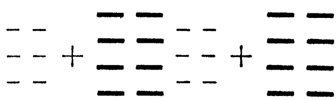
Repulsion.



Attraction.



Repulsion.



Attraction.

It seems possible that an interpretation of some of the most important quantum mechanical results relating to molecular forces could be worked out, which would enable chemists to solve their particular problems with the aid of rules determining the behaviour of electron clouds. These rules would be simple and approximate and utilisable in their proper sphere in much the same way as that in which Faraday used the lines of force, or van 't Hoff the rigid directed bond. It is to be hoped that the possibility of constructing some such theory will be investigated.

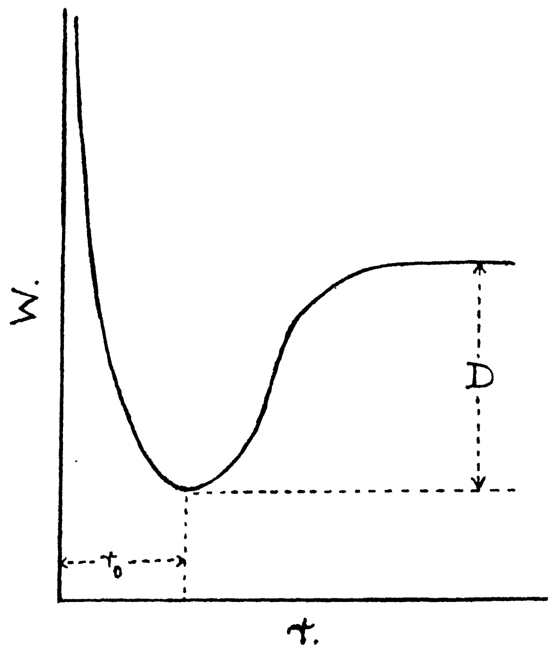
Potential-energy Curves and their Applications.

For the interpretation of the physical and chemical behaviour of diatomic molecules consideration of the potential-energy curve is often of great help. This curve (Fig. 1) represents the potential energy of the molecule as a function of the distance between the atoms, and has the form shown in the figure. At the point where $r = r_0$ the energy is a minimum and the molecule is in its normal equilibrium state. When it is vibrating the atoms may be at

[16] *Proc. Roy. Soc.*, **1931**, [*A*], **133**, 668.

distances greater or smaller than r_0. For the smaller separations the energy increases very rapidly towards indefinitely great values, since the compressibility of a molecule is very limited. As the separation of the atoms exceeds the equilibrium value the energy increases at first fairly rapidly and in approximate accordance with the law of a simple harmonic oscillator, and then more slowly as the binding forces between the atoms get weaker and weaker. Finally the energy reaches a constant limiting value corresponding to complete dissociation of the molecule. The distance D in the figure represents

FIG. 1.



the energy of dissociation. An exact theoretical equation for the form of this curve is hardly possible to obtain, since it will depend upon the variation of binding force with distance, but various semi-empirical equations are used, the constants in which can be evaluated by the aid of data obtained from band spectroscopy. One of the most convenient of these equations is that of P. M. Morse [17] which will be briefly explained, since it is likely to become of increasing importance in chemical calculations.

The energy of the molecule is represented by the expression

$$E(r) = De^{-2a(r-r_0)} - 2De^{-a(r-r_0)}$$

[17] *Physical Rev.*, 1929, **34**, 57; *A.*, 1929, 975.

$E(r)$ is the energy for a displacement r of the two atoms, D is the dissociation energy, and a is a constant.

This expression possesses the following properties : as r approaches ∞, E comes asymptotically to the value zero, *i.e.*, the energy of the completely separated atoms is taken as the standard level; E has a single minimum of $-D$ at $r = r_0$; when $r = 0$ the value of E, although not infinite as it should be, is very great, which is a good enough approximation. Thus the general shape of the curve is provided for. The equation has a further important property : if we write down Schrödinger's wave equation for an oscillator and substitute the above value for the potential energy and then determine the allowed values for the various energy levels of the vibrating system, we obtain a series of the same form as one of the best of the empirical spectroscopic equations. The constants of the two expressions can be equated, and thus a can be expressed in terms of spectroscopic data. For the nth level Morse's equation gives $W(n) = h\omega_0(n + \frac{1}{2}) - (h^2\omega_0^2/4D)(n + \frac{1}{2})^2$. The spectroscopic vibrational levels can be well expressed by the formula $W(n) = h\omega_0[(n + \frac{1}{2}) - x(n + \frac{1}{2})^2]$: ω_0 is the frequency of oscillations small enough to be simple harmonic; from the original equation it is easily found to be equal to $\frac{a}{2\pi}\left(\frac{2D}{\mu}\right)^{\frac{1}{2}}$, where μ is the "reduced mass." After equation of constants and simplification, the value finally found for a is $0{\cdot}2454(M\omega_0 x)^{\frac{1}{2}}$, where $M = M_1M_2/(M_1 + M_2)$, M_1 and M_2 being the atomic weights of the two nuclei on the oxygen scale and ω_0 being expressed in wave numbers. Morse also gives an empirical rule for finding r_0, *viz.*, $r_0^3\omega_0 = 3000$ Å.^{3}/cm. : the latter, however, is not regarded as of universal validity.

Among the applications of the potential-energy curve, we may first consider the approximate estimation of the energies of activation of chemical reactions. Reference was made in the last Report [18] to the calculations of Villars. The idea underlying these has been extended and modified by Eyring and Polànyi, in a series of very interesting calculations based on the London theory of valency and of intermolecular forces.[19] The force between two atoms is made up of two parts : an electrostatic part called the Coulomb force, and a force depending on the quantum mechanical phenomenon of resonance,[20] and going by the name of the "exchange force." In very simple examples the magnitude of these forces can be estimated. In molecule formation the exchange force is the more important. In

[18] *Ann. Reports*, 1930, **27**, 19.

[19] H. Eyring and M. Polanyi, *Z. physikal. Chem.*, 1931, [*B*], **12**, 279; *A.*, 688; H. Eyring, *J. Amer. Chem. Soc.*, 1931, **53**, 2537; *A.*, 1140.

[20] *Ann. Reports*, 1930, **27**, 14.

calculating an energy of activation we must be able to estimate the forces acting between a number of atoms present together: *e.g.*, between three atoms when we are considering a reaction of the type Y + XZ = YX + Z; or between four atoms in a reaction of the type WX + YZ = WZ + XY. As we have just seen, information about the energy of diatomic combinations can be derived from the band spectra of the diatomic molecule; the next step is rendered possible by some formulæ of London's which give the total energy of a system of three or four atoms in terms of the energies which these atoms would possesss if they existed as isolated pairs (diatomic molecules) with nuclear separations equal to their actual distances apart in the polyatomic configuration. For three atoms the total energy is given by

$$E = Q + [\tfrac{1}{2}\{(\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2\}]^{\frac{1}{2}}$$

where $Q = A + B + C$, the sum of the three Coulomb energies of the three atoms taken in pairs, and α, β, and γ are the exchange energies of the three possible isolated molecules. For four atoms the expression becomes

$$E = Q + [\tfrac{1}{2}\{(\alpha_1 + \alpha_2 - \beta_1 - \beta_2)^2 + (\alpha_1 + \alpha_2 - \gamma_1 - \gamma_2)^2 + (\beta_1 + \beta_2 - \gamma_1 - \gamma_2)^2\}]^{\frac{1}{2}}$$

where Q is the sum of six Coulomb energies, and α_1, α_2, . . . , etc., are the exchange energies of the six diatomic combinations. To proceed further some rather bold approximations are necessary. The total energies of the diatomic combinations are first obtained from the band spectra of the corresponding molecules. A rough estimate, based upon the analogy of very simple cases such as H_2 where actual calculation is possible, is then made of the proportion of the total energy which is Coulomb energy and the proportion which is exchange energy: thus the separate terms of the above formulæ are found. To assume that the proportion is constant for different distances of the atoms is obviously a rough and ready procedure, but is more or less justified by the fact that the Coulomb energy is in general only a small fraction of the total. We now can calculate in principle the total energy of any configuration of three or four atoms and can thus study its variation as one molecule approaches another from a great distance and comes into chemical reaction with it. The results of such a calculation are as follows. If we start with XZ at the normal molecular distance, and Y far removed, and then bring up Y, the energy increases : it passes through a maximum and can then fall again if, for example, Z is removed to infinity leaving the molecule YX behind. The "reaction" which has occurred has involved passage over an "energy pass." The minimum height which can be found for this pass for any separation and

direction of approach is the energy of activation of the reaction. Corrections for change in the zero point energy of the molecules which accompanies the reaction must also be applied in a rough manner. The calculation of the course of the energy as the molecules approach for "reaction" is simplified by the fact that London showed in a general way that reactions of the type Y + XZ require least activation when the three atoms remain in a straight line. Eyring and Polanyi have estimated the heats of activation of the reactions H_2 (*para*) + H = H_2 (*ortho*) + H; H + HBr = H_2 + Br; and H + Br_2 = HBr + Br. For the first they obtain 13 kg.-cals., for the second 10, and for the third zero. For the first the experimental value is uncertain but lies between 4 and 11 kg.-cals.; the second and third are merely known to belong to the class of atomic reactions with very small inertia.

Eyring has made similar calculations for reactions of the type $H_2 + X = HX + H$; $H + X_2 = HX + X$; $X_2 + X' = XX' + X$ where X is a halogen. The numerical results are very uncertain because it is necessary to assume *ad hoc* that the Coulomb energy is 3·5% of the total energy and the figure assumed makes a good deal of difference. The most interesting result, however, is a comparative one independent of this assumption; namely, that the reaction between molecular iodine and hydrogen should occur more easily than the reaction by way of iodine atoms, whereas with the other halogens the atomic mechanism is energetically preferred. This of course is in striking accord with experiment.

This is a convenient place to refer to the theory of adsorption catalysis of M. Born and J. Franck and M. Born and V. Weisskopf,[21] which, although not making use of actual potential-energy curves, depends upon general theoretical considerations concerning the potential energy of molecules in relation to the atomic separations. The idea underlying the theory can be illustrated by an analogy. In a homogeneous collision reaction two molecules must meet possessing the energy of activation; quantum mechanically there is a finite probability of transformation by leakage [22] whether they possess this energy or not. But during the short time of a collision the probability is vanishingly small unless the energy is practically equal to or greater than the activation energy: when adsorbed on a surface the sojourn of molecules in proximity to one another is long enough for the probability of transformation to attain a finite value. The theory is thus a combination of the old chemical idea that the surface keeps in proximity molecules which otherwise would have little opportunity to react and the principle underlying the Gamow

[21] *Z. physikal. Chem.*, 1931, [*B*], **12**, 206; *A.*, 576.
[22] *Ann. Reports*, 1930, **27**, 26.

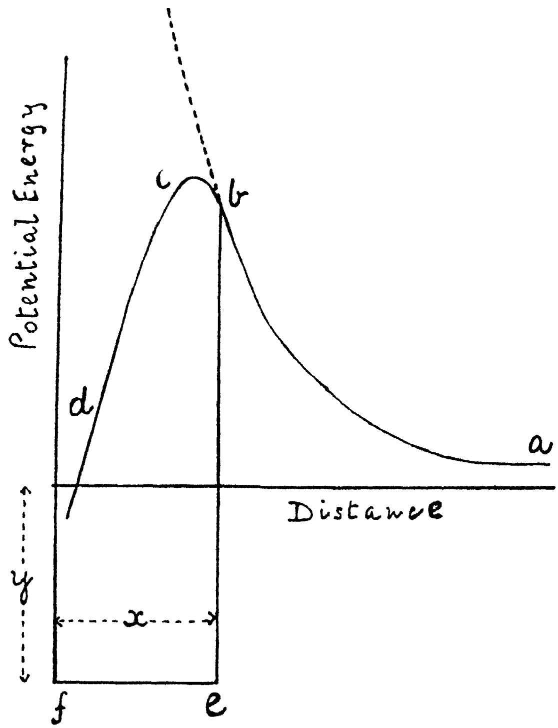
theory of radioactive change with its extensions to the spontaneous chemical changes in molecules.[23] Born and Weisskopf take an idealised picture of a molecular rearrangement, namely two mass points acting on each other with forces and capable of existing in two positions of stable equilibrium at different separations. Thus there will be two sets of states corresponding to various energy levels of the initial and final products of the quasi-chemical rearrangement. If there were no interaction between the two sets of states the Schrödinger equations for them would be independent, but a perturbation term is introduced on account of the mutual potential energy of the atoms and the crystal surface on which they are assumed to be adsorbed. When there are two energy levels, one in the initial set and one in the final set, which correspond, transition by quantum mechanical resonance occurs. The exact correspondence of energy would be extremely unlikely without the crystal surface, which may act in one of two ways. It either takes up itself the difference between the two energies, or it makes the transition possible in virtue of the strong and variable mutual potential energy between atoms and surface. A rather elaborate calculation leads to the result that the probability of transition depends very markedly on the displacement which the atoms have to suffer in the process. If this is of the order of 0·5 Å. it appears that the transformation can occur in a few seconds. To arrive at this result special assumptions have to be made about the oscillation quantum numbers. The authors remark that this picture of adsorption catalysis is not the only possible one : " lowering of the energy threshold, resolution of chemical linkages under the influence of the adsorption forces, intermediate reactions with the atoms of the surface, etc., may be essential factors." It must be remarked here that the experimental evidence has already shown that all these factors and especially the first are in fact of great importance. How much room this leaves for the operation of the quantum mechanical leakage phenomenon is a difficult question.

A very different but equally interesting type of potential-energy curve is that representing the potential energy of an α-particle in the neighbourhood of a nucleus. When the distance is greater than about 10^{-12} cm., the particle is repelled in accordance with Coulomb's law, and the potential energy is represented by the part *ab* of the curve sketched in Fig. 2. For smaller distances the curve must follow a course such as *bcd*, eventually passing into the region of " negative energy," since α-particles inside nuclei are in fact in a stable condition, and under the influence of attractive rather than repulsive forces.[24] The shape of the curve nearer to the centre of

[23] Compare *Ann. Reports*, 1930, **27**, 26, 317.
[24] G. Gamow, " Constitution of Atomic Nuclei," Oxford, 1931.

the nucleus than *b* is a fascinating question connected with the most fundamental problems of nuclear structure and stability. At present only rough and tentative guesses can be made, but even these are proving helpful. For example, the course *abef* may be postulated as an approximation, the potential energy being supposed to drop suddenly to the value in the stable position. The two characteristic magnitudes are then x and y in the figure. H. M. Taylor,[25] working on this basis, has shown that Rutherford

FIG. 2.



and Chadwick's results on the deviations of α-particle scattering in helium from that required by the Coulomb law can be accounted for if suitable values are chosen for the two constants x and y. Knowing these, the energy of binding of an α-particle inside a nucleus can be estimated: here, however, the result is not quite satisfactory, showing that the schematic simplification is too great or is of an inappropriate form. It turns out that the energy lost when two α-particles unite to form a nucleus of mass 8 would correspond to a mass defect of 0·28%, which is very much too

[25] *Proc. Roy. Soc.*, 1931, [*A*], **134**, 103.

large, compared with the known mass defects of elements such as carbon and oxygen.

Liquids and Solutions.

Work continues on the properties of " intensively dried " liquids. The fundamental experimental fact, stated without prejudging any theoretical issue, is that a liquid which has been sealed up with phosphorus pentoxide for a considerable time frequently will not give a rapid continuous stream of vapour unless it is heated to a considerably higher temperature than would have been necessary before the drying process. This means either that some inner equilibrium in the liquid has been displaced, or that the rate of evaporation from the liquid surface has been considerably lowered, rendering the liquid very liable to what is virtually superheating.[26] On general theoretical grounds the latter alternative appears much more probable, since it is easy to understand that during the storage with phosphorus pentoxide either something (such as water or colloidal dust particles) is removed which would have facilitated evaporation, or that something (such as phosphorus pentoxide itself) is introduced which by concentrating itself in the surface layer impedes the free passage of molecules into the vapour phase. The former alternative would be very surprising from the thermodynamic standpoint, since it would mean that a small quantity of a foreign substance produced a change in free energy of the system out of all proportion to that produced by further additions. This would be extremely remarkable since thermodynamic functions in general are linear in the concentration for small additions. From a kinetic point of view it would also be remarkable, since if a very small addition of water produced a finite shift in equilibrium through the bulk of a liquid phase it would mean that each water molecule exerted an influence far beyond the range of ordinary molecular forces. This could only happen by some kind of transmitted polarising effect, the existence of which would imply that liquids possess a " structure." J. W. Smith [27] has recently studied the distillation of ethyl bromide from one evacuated bulb to another across a constant-temperature gradient, and finds that the rate decreases considerably as the " drying " of the liquid proceeds.[28] The vapour pressure, however, remains unaltered, and moreover, there is no evidence of any fractionation of the dried liquid during

[26] Compare *inter alia* E. Cohen and W. A. T. Cohen-de Meester, *Proc. K. Akad. Wetensch. Amsterdam*, 1930, **33**, 1003; *A.*, 294; S. Lenher, *J. Physical Chem.*, 1929, **33**, 1579; *A.*, 1929, 1372.

[27] *J.*, 1931, 2573.

[28] Compare the work of R. Stumper, *Kolloid-Z.*, 1931, **55**, 310; *A.*, 906, on the acceleration of evaporation by colloidal matter.

distillation, such as would be expected if a shift in an inner equilibrium had occurred. This observation is parallel to that of Rodebush and Michalek, who some time ago observed that the rate of evaporation and of condensation of ammonium chloride were diminished by a process of drying. The earlier observation of Smith and Menzies that dry calomel had zero vapour pressure also means that the rate of evaporation was zero under the conditions of the experiment rather than that the equilibrium value had been reduced to nought. There are two analogies, differing in principle, in terms of which these various results may be explained. One is the apparent zero value of the vapour pressure which would be found for slightly contaminated mercury at ordinary temperatures, the other is the complete non-efflorescence of a perfect salt hydrate crystal in the absence of nuclei.

The literature contains a number of conflicting results about the influence of drying on static properties such as surface tension and vapour pressure. (Miss) E. J. Greer [29] found that the addition of very minute traces of water to well-dried benzene gave rise to a partial pressure of several mm. at 20° : this would indicate that a measurable change in the total vapour pressure may occur without the shifting of any equilibrium in the "dried" liquid itself. A. W. C. Menzies,[30] on the other hand, finds that it is quite easy by simple distillation to free benzene from water to such an extent that further changes in vapour pressure on further drying are negligible. S. L. Wright, junr., and Menzies [31] have also failed to confirm the existence of delays in the establishment of vapour-pressure equilibrium, or to find an influence of pre-treatment on the boiling points of such liquids as benzene, carbon tetrachloride, and bromine. W. A. West and Menzies [32] explain Baker's results with acetic acid, where changes of vapour pressure were observed during several days, as due to fractionation of a liquid containing some water. Smits and others [33] have recently shown that the complete removal of dissolved gases from liquids is a much more difficult matter than had been previously supposed. This raises the question whether a number of earlier observations on the change of vapour pressure on drying are not really to be explained by the presence of permanent gases. Repetition of some of the earlier experiments has failed to show any change in the vapour

[29] *J. Amer. Chem. Soc.*, 1930, **52**, 4191; *A.*, 34.
[30] *J. Physical Chem.*, 1931, **35**, 1655; *A.*, 901.
[31] *J. Amer. Chem. Soc.*, 1930, **52**, 4699; *A.*, 1931, 294.
[32] *J. Physical Chem.*, 1929, **33**, 1893; *A.*, 1930, 145.
[33] A. Smits, E. L. Swart, P. Bruin, and W. M. Mazee, *Z. physikal. Chem.*, 1931, **153**, 255; *A.*, 430.

pressure when adequate precautions are taken to free the liquids from gases.

While no doubt a number of unexplained observations remain, the impression grows in strength that changes in static properties of liquids on "drying" are usually spurious effects, while the dynamic effects are genuine but not more mysterious than other influences of nuclei, surface films, or catalysts.

If some of the statements in the literature about the influence of excessively minute traces of impurity on the physical properties of liquids are true, then it is difficult to escape the conclusion that something of the nature of a structure exists in certain liquids under suitable conditions, and that influences from a single molecule are transmitted by some kind of polarising influence, affecting strings or clusters of molecules. Experimentally the situation is not unlike that prevailing in psychical research where, we are told, most of the evidence can be ruled out, but a small obstinate residuum has to be contended with.

A matter of considerable interest in connexion with this general question of the structure of liquids is the possible existence of two liquid forms of certain substances. Two liquid forms of helium [34] with a transition temperature depending on the pressure have been described. From discontinuities in the curves showing the variation with temperature of such properties as density, specific heat, viscosity, and dielectric constant, the existence of two liquid forms of nitrobenzene,[35] carbon disulphide,[36] and ether [37] has been inferred. But with nitrobenzene,[38] at least, careful re-investigation of the problem indicates that the effects claimed are not real. It is to be hoped that the phenomenon will be quite definitely established as real in certain examples or explained away in the near future.

Among the most clarifying advances of the last ten years in physical chemistry has been the recognition of the part played by purely electrostatic forces in determining the properties of dilute solutions of electrolytes. Conductivity, osmotic pressure, and the thermodynamic properties deducible from it, mutual solubility influences of electrolytes, and the so-called salt effect on reaction velocity all depend to a greater extent on the interionic forces than on any other single factor : indeed, the Debye–Hückel theory

[34] W. H. Keesom and K. Clusius, *Naturwiss.*, 1931, **19**, 462; *A.*, 1004; *Proc. K. Akad. Wetensch. Amsterdam*, 1931, **34**, 605; *A.*, 1004.

[35] J. Mazur, *Nature*, 1930, **126**, 993; 1931, **127**, 741, 893; *A.*, 1931, 148, 792, 899.

[36] M. Wolfke and J. Mazur, *ibid.*, p. 926; *A.*, 896.

[37] J. Mazur, *ibid.*, 1930, **126**, 649; 1931, **127**, 270; M. Wolfke and J. Mazur, *ibid.*, 1930, **126**, 684.

[38] N. B. Massey, F. L. Warren, and J. H. Wolfenden, *J.*, 1932, 91.

of electrostatic interaction is so closely followed by many strong electrolytes at high dilution that deviations from it can now be regarded, not so much in the light of a failure of a theory as of useful positive information about the intrusion of other specific factors. These specific factors do in fact continue to reveal themselves in a number of instances. For example, among the more recent results are the following: in nitromethane solution tetraethylammonium salts behave in agreement with the Debye–Hückel–Onsager theory of conductivity, but other salts, which behave as strong electrolytes in alcoholic solution, are weak electrolytes in nitromethane [39] in spite of its greater dielectric constant. Thus molecule formation is by no means controlled by electrostatic forces, even though the behaviour of ions can be predicted in terms of them if molecule formation does not actually occur.

Two further important consequences of the Debye–Hückel theory of interionic forces in dilute solutions have been investigated. The first, relating to the viscosity of dilute solutions of electrolytes, is explained in another section of the report. The second is that in dilute solution the partial molar volume of an electrolyte, or the related quantity, the apparent molecular volume, is proportional to the square root of the concentration. In 1929 Masson [40] showed that such a square root relation held for a number of electrolytes, and later W. Geffcken [41] elaborated the matter. O. Redlich and P. Rosenfeld [42] have now shown that such a relation is a necessary consequence of the Debye–Hückel theory. They derive the equation

$$\overline{V}_2 = \overline{V}_2^0 + qw^{3/2} \, . \, c^{1/2}$$

$\overline{V}_2^0$ is the limiting value of the partial molar volume $\overline{V}_2$ at infinite dilution; $w = \frac{1}{2}\Sigma\nu_s z_s^2$, where ν_s = number of ions of kind S per molecule, and z is the valency of the ion; q is a constant depending upon the temperature, the dielectric constant of the solvent, the variation of the dielectric constant with pressure, and the compressibility of the solvent. The "apparent molecular volume," ϕ, is related to the "partial molar volume" by the relation $m\overline{V}_2 = \frac{d(m\phi)}{dm}$, where m = the number of g.-mols. of solute per 1000 g. of solvent. For ϕ the following equation holds: $\phi = \phi^0 + \frac{2}{3}q \, . \, w^{3/2} \, . \, c^{1/2}$.

From the examination of the experimental data made by Masson

[39] C. P. Wright, D. M. Murray-Rust, and (Sir) H. Hartley, *J.*, 1931, 199; compare also the results for nitrobenzene, W. F. K. Wynne-Jones, *ibid.*, p. 795.

[40] (Sir) D. O. Masson, *Phil. Mag.*, 1929, **8**, 218.

[41] *Z. physikal Chem.*, 1931, [*A*], **155**, 1.

[42] *Ibid.*, p. 65; *Z. Elektrochem.*, 1931, **37**, 705.

and by Geffcken, the square-root relation appeared to hold for a given electrolyte up to fairly high concentrations, but the slope of the curves exhibiting the relation varied from example to example in an apparently individual manner. Redlich and Rosenfeld, examining the best experimental data, come to the conclusion, however, that at higher concentrations the lines are really curved and that at great dilution they all converge to a single straight line, with the anticipated slope. While the best test can be made with the data for uni-univalent electrolytes, the influence of the valency factor with multivalent electrolytes is, as far as can be seen, approximately in accordance with the theory. Examination of data for methyl-alcoholic solutions indicates that the influence of the solvent on the constant q can also be accounted for.

There is no doubt that electrostatic forces may play a considerable part in determining solubility, but it is also clear that their influence is only one among many factors. By comparing theoretical predictions of solubility, based upon a purely electrostatic theory, with the experimentally found relations, an idea can be formed of the importance of the electrical factor. The general principle underlying such calculations is as follows. Some simple model of an ion or molecule is adopted and its electrical energy in a medium of given dielectric constant is worked out. The difference between the electrical energies it possesses in two different media is then equated to the work of transfer from one medium to the other, *i.e.*, to $kT \ln K$, where K is the partition coefficient. Such calculations are successful only in a very general and qualitative way for ionic partition coefficients. R. P. Bell[43] has recently extended them to the solubility of dipole molecules, and thus obtained an interesting picture of the extent to which the electric moment of such molecules determines their behaviour. As a model he assumes a spherical molecule of dielectric constant unity, with a dipole at its centre, the distance between the two charges of the dipole being small compared with the radius of the sphere. He points out that only in rather extreme examples can the treatment give quantitative results, since it would predict, for example, equal solubilities for non-polar gases such as hydrogen, oxygen, and nitrogen. With strongly polar molecules, such as ammonia and water, there is a much better chance of success, and Bell finds for the relative solubilities of these two substances in a number of solvents a dependence upon the dielectric constant agreeing fairly well with that anticipated by the theory, especially for the solvents of higher dielectric constant.

For the solubility of the mercuric halides, regular relations are

[43] *J.*, 1931, 1371; *Trans. Faraday Soc.*, 1931, **27**, 797.

also found. The conditions under which the method of calculation is more or less adequate appear to be, therefore, when the dipole moment of the solute is large, the dielectric constant of the solvent is large, and also when the dipole molecule itself has a large diameter, since then the approximation involved in regarding the solvent as a continuous medium is better justified.

As exemplified by examples referred to in a later section, the electric moment of molecules does not appear to determine their adsorption on surfaces to any important extent. However, as might be expected, the degree of ionisation of a dissociable group in an interface influences the interfacial tension to a marked degree. The interfacial tension between aqueous and benzene solutions of the higher fatty acids varies with the hydrogen-ion concentration of the aqueous phase over just the range which would be expected if it were determined by the degree of ionisation of the unimolecular interfacial layer, although in certain examples specific effects are superimposed. R. A. Peters [44] has recently shown that the interfacial tension of the system benzene–water–hexadecylamine varies with hydrogen-ion concentration in just the opposite sense to that for the long-chain acids, but over approximately the same range, and indeed that the interfacial-tension changes follow rather closely the dissociation curve for a weak base. Here, therefore, we have another example of a phenomenon where electrostatic forces are of predominant importance.

The Viscosity of Solutions of Electrolytes (by H. W. Thompson).

Measurements of the viscosity of dilute solutions of electrolytes have recently acquired considerable theoretical interest. The Debye–Hückel interpretation of the conditions existing in such solutions, and the theoretical derivation of the Kohlrausch square-root relation between equivalent conductivity and concentration were based upon the idea that in the neighbourhood of any ion there will be more ions of unlike than of like sign. The "ionic atmosphere" will normally be symmetrical, but will become distorted when the central ion moves. It possesses a "thickness" and requires a definite time for its establishment—these magnitudes being determined by the ionic concentrations, the valencies, the temperature, and the dielectric constant of the solvent. The velocity of the central ion, moving under the influence of an electric field, will depend on the properties of the atmosphere.

It is not unnatural to suppose that the ionic atmosphere plays a part in determining the viscosity and in particular its variation with salt concentration.

[44] *Proc. Roy. Soc.*, 1931, [*A*], **133**, 140.

The viscosity of liquids and solutions has been studied experimentally for a long time. Earlier workers confined themselves primarily to the construction of reliable viscometers : later work dealt primarily with the connexion between viscosity and molecular structure, and with questions such as that of molecular association. Hübner first investigated the viscosities of a series of salt solutions and found that addition of salt sometimes decreased the viscosity of the solvent. Sprung concluded that salts could be divided into two groups : those of the first depress the viscosity of water at low temperatures but increase it somewhat at higher temperatures, while those of the second group always increase the viscosity. The work of Slotte, Arrhenius, Wagner, Ranken, and Taylor and Getman led to the suggestion of various empirical relationships expressing the coefficient of viscosity, η, as a function of the concentration. Grüneisen,[45] working at greater dilutions, discovered that the curves of viscosity plotted against concentration exhibit a negative curvature at the dilute end. He attempted, but not very satisfactorily, to explain the results in terms of the electrolytic dissociation theory. M. P. Applebey [46] confirmed the existence of " negative curvature " and also the fact that electrolytes may cause either an increase or a decrease in the viscosity of the solvent. He suggested that two opposing factors operate in determining the viscosity of a solution : on the one hand, there is a depolymerisation of triple water molecules which tends to decrease viscosity, and on the other, there is ionic friction which increases it. With feebly hydrated ions the second factor will be small compared with the first, and accordingly a net decrease in viscosity will be observed. In general, however, ions will be hydrated to such an extent that, at any rate at the higher dilutions, a net increase of viscosity will be found.

G. Jones and M. Dole [47] have recently redetermined the viscosities of solutions of barium chloride at various concentrations. Their results are not in agreement with any of the earlier empirical relationships. While at the higher concentrations there is a certain degree of proportionality between fluidity (reciprocal viscosity) and concentration, yet at the lower ones, *i.e.*, in the region of the so-called negative curvature, a systematic discrepancy exists. Jones and Dole propose to account for this qualitatively as follows. According to the Debye–Hückel theory of the ionic atmosphere, the effect of the interionic forces in opposing the motion of an ion in an electric field is proportional to the square root of the concentration

[45] *Wiss. Abhandl. Techn. Reichsanstalt*, 1905, **4**, 151, 237.
[46] *J.*, 1910, **97**, 2000.
[47] *J. Amer. Chem. Soc.*, 1929, **51**, 1073, 2950; *A.*, 1929, 767, 1385.

in very dilute solutions. Thus for the fluidity the following relationship is indicated : $\phi = 1 + A\sqrt{c} + Bc$. For all strong electrolytes, A will have a negative value (the fluidity decreasing with concentration), and for non-electrolytes it will be zero; B can only be regarded in the first instance as an empirical coefficient. The relation can be re-expressed as $(\phi - 1)/\sqrt{c} = A + B\sqrt{c}$, or if the higher concentration term be neglected, $\eta/\eta_0 = 1 + K\sqrt{c}$, where K is a fresh coefficient. The latter form is now most common.

Jones and Dole re-examined the older data, which appeared to obey the relation, although there is a lack of data for high dilutions. They accordingly predicted that at high dilutions the viscosity of solutions of all strong electrolytes will be greater than that of pure water even in the case of salts which at ordinary concentrations show a diminution of viscosity. This requirement was already satisfied by the results of K. Schneider [48] working with solutions of potassium chlorate : an increase in viscosity occurred between 0 and 0·05N, but at higher concentrations a falling off was observed. The same is true of nitric acid solutions, where W. Bousfield [49] found that at 11° and below $N/32$ the viscosity exceeds that of water. At higher temperatures the viscosity exceeded that of water at all concentrations examined.

A mathematical investigation of the problem from the standpoint of the Debye–Hückel theory enabled H. Falkenhagen and M. Dole [50] to derive the relation $\eta/\eta_0 = 1 + K\sqrt{c}$. The simple case of a uni-univalent electrolyte with ions of equal mobility was first studied. The calculation leads to the result

$$K = \{e/60\eta_0 u\sqrt{DkTz}\} \times 0{\cdot}491 \times 10^{10},$$

where e is the electronic charge, η the viscosity of the solvent, u the reciprocal of the frictional force acting on the ions, D the dielectric constant of the solvent, k the Boltzmann constant, T the absolute temperature, and z the valency of the ions. H. Falkenhagen has recently extended the calculations to include any single salt.[51]

The only salt with ions of approximately equal mobility is potassium chloride, for which the calculated value of K is 0·0046. A series of theoretical values for various salts are given by Falkenhagen and Dole. W. E. Joy and J. H. Wolfenden [52] have now confirmed the value of K predicted for solutions of potassium

[48] *Diss.*, Rostock, 1910. [49] *J.*, 1915, **107**, 1781.

[50] *Physikal. Z.*, 1929, **30**, 611; *A.*, 1929, 1389; *Z. physikal. Chem.*, 1929 [*B*], **6**, 159; *A.*, 1930, 155; also H. Falkenhagen, "Reviews of Modern Physics," 1931, **3**, 412; *Nature*, 1931, **127**, 439; *A.*, 560.

[51] *Z. physikal. Chem.*, 1931, [*B*], **13**, 93; *A.*, 905; *Physikal. Z.*, 1931, **32**, 365; *A.*, 686.

[52] *Proc. Roy. Soc.*, 1931, [*A*], **134**, 413.

chloride, nitric acid, rubidium nitrate, and potassium chlorate. Some earlier determinations of the viscosity of rubidium nitrate solutions by H. G. Smith, J. H. Wolfenden, and (Sir) H. Hartley [53] also exhibit the Falkenhagen–Dole effect. This effect provides a further confirmation of the idea of the ionic atmosphere, and the influence of electrostatic forces in determining the properties of dilute solutions.

Surface Chemistry.

So many papers have been devoted to various aspects of surface chemistry that it is necessary to devote a section again this year to a few at least of the divisions of this rapidly expanding subject.

The explanation of the nature of adsorptive forces in terms of the newer theories of molecular forces has been discussed by F. London and M. Polanyi.[54] It appears, as one might have expected, that the dipole moment of the adsorbed molecule is of secondary importance only in adsorption phenomena, a conclusion which is supported by the experiments of H. Cassel and F. Salditt [55] on the adsorption of various vapours by mercury. It is also of interest to note in this connexion that C. A. Sloat and A. W. C. Menzies [56] find the adsorption of various alkali bromides by lead sulphide not to be related in any way to the lattice dimensions of the deposited salt. Three of the six salts examined give orientated deposits on lead sulphide, but there appeared to be no preferential adsorption of these. Among many other papers on the more general aspects of adsorption phenomena may be mentioned a detailed discussion of the nature of the boundary layer in " lubrication " phenomena by Sir W. Hardy,[57] in which chains of highly polarised molecules stretching from one of the solid surfaces to the other are pictured.

A general theory of the quantum mechanics of adsorption catalysis is dealt with in another section. B. Topley [58] has also derived a theoretical expression for the rate of a heterogeneous gas reaction, using assumptions analogous to those employed in the consideration of homogeneous reactions : the results generally are in good agreement with experiment. Even if the details of Topley's calculation are not accepted in their entirety, his results seem to show that the introduction into the theory of adsorption catalysis of quantum mechanical " leakage " effects is far from necessary.

On the whole, much more work has been done on adsorption considered as a statical (equilibrium) phenomenon than on the

[53] *J.*, 1931, 403. [54] *Naturwiss.*, 1930, **18**, 1099; *A.*, 1931, 161.
[55] *Ibid.*, 1931, **19**, 110; *A.*, 421.
[56] *J. Physical Chem.*, 1931, **35**, 2022; *A.*, 904.
[57] *Phil. Trans.*, 1931, [*A*], **230**, 1; *A.*, 559.
[58] *Nature*, 1931, **128**, 115; *A.*, 918.

dynamical aspect of the process. We may, however, now consider some papers dealing with this important side of the subject. Experiments on the exchange of energy between helium atoms and surfaces of tungsten and of nickel are described by J. K. Roberts,[59] the method of investigation being that of studying the heat loss from a wire of the metal surrounded by the gas. The accommodation coefficient is found to vary with the state of adsorbed gas films on the wires. T. Alty,[60] by measuring the rate of evaporation from a water surface and extrapolating to zero pressure, obtains the ideal rate of evaporation into a vacuum: by comparing this with the rate at which molecules strike the surface from the saturated vapour it is found that, in order that there may be equilibrium, only about 1% of the incident molecules actually enter the liquid. G. Veszi[61] estimates that when the atoms in a metal vapour are reflected from the surface of a stream of oil, they sojourn in some cases for a period of the order of 10^{-4} to 10^{-5} sec. on the oil surface. An interesting relation between catalysis and accommodation comes to light in the work of K. F. Bonhoeffer and A. Farkas[62] on the transformation of para-hydrogen into the equilibrium mixture under the influence of a heated platinum wire. The suggested mechanism of the catalysis is that the para-hydrogen is adsorbed by the metal in the atomic form, and that re-evaporation in the molecular form subsequently takes place, ortho- and para-hydrogen naturally coming off in the equilibrium proportion. The usual platinum catalytic poisons inhibit the transformation, while a trace of oxygen accelerates it. Now at lower temperatures, where no catalysis occurs, heat exchange between the wire and the gas takes place only by the process of reflexion of molecules from the surface. But at higher temperatures adsorption of the striking molecules and their subsequent evaporation play a considerable part in the energy exchange, and one finds that the accommodation coefficient, as inferred from the amount of electrical energy required to maintain the wire at a given temperature, increases abnormally, and that this increase sets in just as the catalytic activity appears. Poisoned platinum at the same temperatures continues to show a normal coefficient.

Under normal conditions both direct experiment and indirect evidence from the kinetics of heterogeneous reactions show that the rate at which an adsorption equilibrium is established is very great. Slow processes are usually interpreted as solution phenomena or

[59] *Proc. Roy. Soc.*, 1930, [*A*], **129**, 146; *A.*, 1930, 1340.
[60] *Ibid.*, 1931, [*A*], **131**, 554; *A.*, 904.
[61] *Z. physikal. Chem.*, 1930, [*B*], **11**, 211; *A.*, 1931, 162.
[62] *Ibid.*, 1931, [*B*], **12**, 231; *A.*, 691.

chemical changes. H. S. Taylor [63] has, however, recently suggested that these slow changes are of more fundamental importance than has hitherto been assumed. He says "there are now numerous data showing abnormal variations in the extent of adsorption with both temperature and pressure, large variations in the velocity of attainment of equilibrium in different adsorption systems and in the velocity of evaporation of adsorbed gases inconsistent with the present adsorption theory." Taylor suggests that true adsorption *per se* is not necessarily a rapid process, but one which takes place with a characteristic velocity determined by the same kind of factors as those which govern the rate of chemical changes, and in particular that an activation energy may in some cases be necessary for a molecule to be adsorbed by a surface. He points out that a diatomic molecule can in principle be adsorbed in two ways, either molecularly or with accompanying resolution into atoms. The first kind of process would be expected to have a very small heat of activation, but the second may well require the absorption of very considerable amounts of energy; it would thus be improbable at low temperatures, but would have a high temperature coefficient. Some of the conclusions which may be drawn from these postulates are as follows. At low temperatures molecular adsorption will predominate, the total amount adsorbed in this way decreasing as the temperature rises. In a certain higher range of temperature the total adsorption increases again, not on account of changed equilibrium conditions, but because the *velocity* of the activated atomic adsorption, hitherto negligible, now becomes appreciable. In this region equilibrium will not be attained instantaneously, and it may be found that the large amounts of gas taken up at a higher temperature are more or less tenaciously retained on rapid cooling to a temperature where they would not originally have been taken up. Furthermore, the heat of adsorption will vary with temperature according to whether the molecular or the atomic type of adsorption is predominating. Some examples of the evidence that effects of this kind are indeed observed may now be quoted. The adsorption of hydrogen by nickel above − 100° is rapid: at lower temperatures, A. F. Benton and T. A. White [64] found the adsorption at a given temperature to vary according as the saturation was effected at the actual experimental temperature or at a higher one with subsequent cooling. Between − 183° and − 191° adsorption was rapid but at higher temperatures it was slower, suggesting according to Taylor's point of view that a process with an activation energy is coming into play. Taylor

[63] *J. Amer. Chem. Soc.*, 1931, **53**, 578; *A.*, 421.
[64] *Ibid.*, 1930, **52**, 2325; *A.*, 1930, 990.

quotes other evidence of a similar kind, such as the diminishing adsorption by platinum as the temperature falls, the "plurality of processes" involved in the fixation of oxygen by charcoal, and the hysteresis phenomena observed in the adsorption of oxygen by silver and gold.

It will be readily admitted that the processes postulated by Taylor may in principle play an important part in adsorption phenomena, and that the conclusions he draws from his postulates are correct. But it is open to considerable doubt at the moment whether the experimental observations which he quotes in his first paper are really to be identified with the operation of such processes. It is necessary first to show that the abnormal temperature influences and the hysteresis effects are not really due to solution. Taylor argues that the amounts of gas involved are higher than the known solubilities, and that in these adsorption effects the surface factor is all important, which it would not be in a solubility phenomenon. But to this must be said that it is not a question of the equilibrium solubility, but rather of rate of solution. At low temperatures the penetration of a gas into the lattice of a metal will in general be excessively slow: at higher temperatures the porosity increases and gas can penetrate a few layers of atoms not far removed from the surface, especially when the surface structure of the metal has been loosened and to some extent opened up by various chemical or physical treatments. Where gas has once penetrated, gas can penetrate again more easily than before, and in the case of a metal which has had the outer layers of its mass opened up, we may have a fairly easy absorption or removal of gas which appears something like the rapid establishment of an equilibrium. But this is very far from being the true solubility: persevering treatment at higher and higher temperatures will make the metal more and more porous. It is improbable that with a massive metal the true solubility would be attained except under quite exceptional conditions, so that Taylor's argument about the magnitude of solubility effects seems inconclusive. Increasingly great ease of penetration of metals by gases as the temperature rises (the penetration being in any case slow and difficult, and, moreover, retarded by the gas already taken up), is a factor which undoubtedly must be taken into account, and which will inevitably mask the effects discussed by Taylor.[65] These important effects ought, however, to exist, and it may be possible with experimental work of some delicacy to isolate them from the other complications, as we shall see below in dealing with some of the most recent work.

(It may be remarked here that failure of the so-called Polanyi–

[65] Compare E. W. R. Steacie, *J. Physical Chem.*, 1931, **35**, 2112; *A.*, 904.

Hinshelwood equation [66] when a measured heat of adsorption is used does not necessarily indicate that another energy term, Taylor's activation energy of adsorption, is to be introduced. According to Taylor's well-established theory of active points, the heat of adsorption on the active points responsible for the catalysis will not bear any definite relation to the average heat of adsorption revealed by a calorimetric measurement.)

In pursuing the idea of activated adsorption, Taylor and Williamson [67] have found some interesting results on the adsorption of hydrogen by manganous oxide and manganous oxide–chromium oxide mixtures. The process is slow with manganous oxide at 0° and 100°, and between 184° and 305° increases in rate ten-fold, corresponding to a " heat of activation " of about 10,000 calories : with the promoted oxide both kinds of adsorption can be studied, one with a negligible " heat of activation " and the other with the high and variable value for this quantity. The adsorption is reversible. W. E. Garner and F. E. T. Kingman [68] find that a catalyst of zinc and chromium oxides adsorbs hydrogen and carbon monoxide at low temperatures " without dissociation of the molecules," whereas above 100° the adsorption becomes irreversible and the gases can only be removed as water or carbon dioxide.

F. E. T. Kingman has also made observations on the critical increment of adsorption of hydrogen by charcoal.[69]

In connexion with the discussion of the part played by actual penetration, rather than surface adsorption, in the processes classed under the general heading of sorption, the work of M. G. Evans [70] on the sorption of ammonia by chabazite is of great interest. He finds that when ammonia is taken up the X-ray diagrams of the chabazite show distortion of the space lattice. This distortion, caused by actual penetration of the ammonia molecules, may ultimately shatter the crystal. While it is not probable that all slow sorption depends upon such effects, this work shows that specific allowance for the possibility of such penetration must be made in any given example.

In certain examples, notably with oxygen and charcoal, the heat of adsorption for the first portions of gas taken up is greater than for subsequent portions. A. F. H. Ward,[71] however, has found that the heat of adsorption of hydrogen by activated copper is independent of the concentration of gas on the surface. In these

[66] J. K. Dixon, *J. Amer. Chem. Soc.*, 1931, **53**, 1763; *A.*, 803; H. Dohse and W. Kälberer, *Z. physikal. Chem.*, 1929, [*B*], **5**, 131; *A.*, 1929, 1231.

[67] H. S. Taylor and A. T. Williamson, *J. Amer. Chem. Soc.*, 1931, **53**, 813, 2168; *A.*, 421, 902.

[68] *Trans. Faraday Soc.*, 1931, **27**, 322.

[69] *Nature*, 1931, **128**, 272.

[70] *Proc. Roy. Soc.*, 1931, [*A*], **134**, 97.

[71] *Ibid.*, 1931, [*A*], **133**, 506, 522.

experiments there was a clear separation observable between the instantaneous adsorption and a slow subsequent process of solution. Ward adduces evidence to show that the dissolved hydrogen is not split up into atoms as has often been supposed, and also gives reasons for supposing that penetration of the copper by the hydrogen occurs by diffusion along the boundaries of metal grains rather than by diffusion into the lattice. These considerations are relevant also in connexion with the above remarks on Taylor's views.

An interesting new method of investigating surface films has been developed by J. H. Schulman and E. K. Rideal,[72] following up a technique introduced by Guyot and by Frumkin. The potential difference at the surface of an aqueous solution bearing a thin film of a substance such as a fatty acid is measured electrometrically, one electrode being a calomel electrode making contact with the liquid in the trough, the other being an air electrode, consisting of a metal plate above the solution with the intervening air gap ionised by a radioactive preparation. The acidity of the aqueous layer can be varied, the state of compression of the film can be altered as in the Langmuir–Adam trough, and the variations in surface potential studied. Theoretically the difference of potential at the surface is given by $\Delta V = 4\pi n\mu$, where n is the number of molecules per sq. cm. of surface and μ is the effective vertical component of the average electric moment. By this method transitions, for example, from vapour to liquid expanded film can be observed. The values of μ in different states of the films can be found and conclusions can be drawn about the structure and configuration of the films. The authors give evidence for the existence of a new phase appearing in the transition from the liquid to the vapour state of films of fatty acids. There are also indications that in the vapour films the molecules are horizontally orientated.

A. J. Allmand and others [73] have continued a detailed and systematic study of the adsorption isotherms of gases and vapours. One of the most important results [74] of the more recent of these investigations is the strong indication found that the adsorption of vapours by porous solids such as charcoal is definitely discontinuous in nature: the curves representing amount adsorbed plotted against pressure of the vapour in the gas phase showing breaks, or even horizontal steps where the amount adsorbed

[72] *Proc. Roy. Soc.*, 1931, [*A*], **130**, 259, 270, 284; *A.*, 299.

[73] A. J. Allmand and R. B. King, *ibid.*, p. 210; *A.*, 160; A. J. Allmand and A. Puttick, *ibid.*, p. 197; *A.*, 160.

[74] A. J. Allmand and L. J. Burrage, *ibid.*, 1931, [*A*], **130**, 610; *A.*, 558; compare also A. F. Benton and T. A. White, *J. Amer. Chem. Soc.*, 1931, **53**, 2807; *A.*, 1005.

increases suddenly for a small increase of pressure. The interpretation of these observations depends upon the fact that the surfaces possess regions of different adsorptive power, and upon the fact that the adsorbed vapour may change from a two-dimensional gas to a two-dimensional liquid at certain critical pressures.

Mention should also be made of the work of N. I. Kobosew and W. L. Anochin,[75] who study adsorbed gas films by the method of electron bombardment, measuring, not the ionisation potential of the adsorbed gas as in the experiments of J. H. Wolfenden [76] and of G. B. Kistiakowsky,[77] but the actual rate at which the gas becomes desorbed under the influence of the electron stream. While the interpretation of some of their observations seems a little speculative, it is interesting to note that Kobosew and Anochin distinguish three " desorption potentials " of hydrogen from platinum, corresponding to the release of the gas from plane surface, edges, and corners of the solid respectively. Complex relations are found when oxygen and hydrogen are simultaneously present on the surface.

Structure of Natural Products.

As an example of the way in which complex natural structures are being investigated, reference may be made to the work of J. B. Speakman [78] on the micelles of wool fibre. The methods used are interesting : the elastic properties of wool fibres in dry air and in water are quite different; fibres in methyl or ethyl alcohol behave as in water, while fibres in butyl or amyl alcohol behave as though dry. Thus the capillary space in the wool fibre is probably of about the same size as the molecule of propyl alcohol, in which liquid an intermediate behaviour is found. When it takes up a liquid, a wool fibre may swell and subsequently be able to take up another liquid which could not have penetrated into the dry wool. By studying the elastic properties of the fibres in mixed liquids, information about the structure of swollen fibres can be obtained. This is supplemented by observations on change of length on swelling, comparison with *X*-ray data, and deductions from various other facts to give a detailed picture. The wool fibres have a " plate-like " structure, and are arranged with their long axes parallel to the fibre length : they are probably about ten times as long as thick. The micellar thickness is about 200 Å., and the intermicellar distance about 6 Å., increasing on swelling in

[75] *Z. physikal. Chem.*, 1931, [*B*], **13**, 63; *A.*, 903.
[76] *Proc. Roy. Soc.*, 1926, [*A*], **110**, 464; *A.*, 1926, 217.
[77] *J. Physical Chem.*, 1926, **30**, 1356; *A.*, 1926, 1188.
[78] *Proc. Roy. Soc.*, 1931, [*A*], **132**, 167; *A.*, 1003.

water to about 41 Å. This makes the internal surface of wool something of the order of a million sq. cm. per gram.

An extremely interesting account of X-ray studies of hair and other animal fibres has been published by W. T. Astbury and A. Street,[79] who find that all animal hairs appear to give substantially the same X-ray diagram. When the hair is stretched, one form of X-ray photograph (the "α") gives place to another (the "β") corresponding to a unit cell of quite changed dimensions. This transformation seems to depend upon the reversible change of a certain group of length 5·15 Å. into another of length 6·64 Å., and plays a very important part in determining the elastic properties of hairs, which are in many ways remarkable. The "β" form is more vulnerable to the attack of sodium sulphide, and in this connexion it is a suggestive fact that the most intense X-ray reflexion given by stretched hair has the same spacing as the most important reflexion which the substance cystine gives. In this work we see, however incompletely, that interrelation of micellar structure, chemical structure and behaviour, and mechanical properties upon which the function of living matter must depend.

Chemical Kinetics.

In the Annual Report for 1927 it was remarked that if the theory of collisional activation in unimolecular reactions proved to be generally applicable, then the distinction between unimolecular and bimolecular gas reactions would become one of degree only. This anticipation is apparently being fulfilled, and the classical division of reactions into orders is losing a good deal of its significance. Naturally in a change of the type $X + Y = XY$ we still have a bimolecular reaction in the older sense, but complications arise in reactions of the types $XY = X + Y$, and $2XY = X_2 + Y_2$. In all known thermal reactions of the first of these two latter types, activation is by collision (though in principle we can hardly yet rule out the possibility that real non-collisional unimolecular changes may be discovered), and thus these changes do not differ in principle kinetically from those of the second type. The essential difference is merely one in the time which elapses between activation and reaction, and therefore in the relative importance of deactivation of the active molecules by subsequent collision before the chemical transformation has occurred. In general we may say: rate of activation $= k_1c^2$; rate of deactivation $= k_2c \, . \, a$, where a is the concentration of active molecules; rate of actual chemical transformation $= k_3a$. For a stationary concentration of active mole-

[79] *Phil. Trans.*, 1931, [*A*], **230**, 75; *A.*, 897.

cules $k_1c^2 = k_2c \cdot a + k_3a$; whence the rate of reaction is $k_3a = k_1c^2/(1 + k_2/k_3 \cdot c)$. According as the ratio k_2/k_3 is great or small, the reaction approximates to the classical unimolecular or bimolecular type. Only when the chance of deactivation is absolutely zero can the reaction remain bimolecular up to indefinitely great pressures. In reactions of the type $2XY = X_2 + Y_2$ this condition might be fulfilled if both molecules had to be transformed at the moment of impact or never, as, for example, when the process $XY = X + Y$ is energetically impossible. Even here, however, deactivation at really high pressures could occur by ternary collision, so that in general we must not expect simple definite orders of reaction, but only approximations to a given order in a given region of pressure. The principle that simple molecules give bimolecular reactions while complex molecules give unimolecular reactions should be stated in the form that complex molecules undergo reactions which become kinetically unimolecular at relatively low pressures while simple molecules react bimolecularly up to relatively very high pressures.

Turning to some of the recent experimental evidence illustrating these ideas, we may first take the decomposition of nitrous oxide. When this was first investigated, a reaction depending upon collision of two molecules was called bimolecular, and unimolecular reactions were supposed to be changes of isolated molecules produced by an agency such as radiation: in this sense the decomposition of nitrous oxide proved to be definitely bimolecular. However, over its whole course the reaction did not give good bimolecular constants, nor did the straight line obtained by plotting the reciprocal of the time of half change against the pressure pass through the origin, as it should in a classically perfect bimolecular reaction: complicating factors were known to exist. N. Nagasako and M. Volmer,[80] making measurements up to pressures of 10 atmospheres, state that the reaction tends to become kinetically unimolecular. H. C. Ramsperger and G. Waddington,[81] treating the reaction as a quasi-unimolecular one, show that only two squared terms are involved in the activation process, so that the reaction still belongs to the category of those with a simple activation mechanism. Whether we should regard the actual process of the chemical transformation at higher pressures as $N_2O = N_2 + O$, or whether the chemical process is still to be regarded as essentially $2N_2O = 2N_2 + O_2$ with a marked deactivation at high pressures by ternary collisions—the binary collisions being assumed to have a small but finite duration—is at the moment an open question.

[80] *Z. physikal. Chem.*, 1930, [*B*], **10**, 414; *A.*, 1931, 174.
[81] *Proc. Nat. Acad. Sci.*, 1931, **17**, 103; *A.*, 571.

If the former is the real mechanism it is very interesting, since at quite low pressures another homogeneous unimolecular decomposition of nitrous oxide has recently been detected.[82] Thus there would be two independent modes of activation of the N_2O molecule. The decomposition of ozone,[83] bimolecular as ordinarily measured in the gas phase at comparatively low pressures, becomes unimolecular in carbon tetrachloride solution. While it is possible that the mechanism of the solution reaction may be quite different (involving a chain process in which the solvent takes part) there is at least an interesting possibility that the solvent merely acts as an enormous concentration of inert gas, and so aids the quasi-unimolecular reaction of ozone to attain its limiting unimolecular rate, the action being analogous to that of hydrogen and other inert gases on certain gas reactions definitely known to be of the quasi-unimolecular variety.

Further interesting examples of quasi-unimolecular reactions have been discovered. In the unimolecular decomposition of germanium tetraethyl,[84] the rate of reaction begins to fall off at about 70 mm. The limiting velocity is given by the expression $\ln k = 32{\cdot}8 - 51{,}000/RT$; 8—10 degrees of freedom appear to be involved in the activation process. The thermal decomposition of dimethyltriazene [85] is a homogeneous reaction of the same type; the rate falls off at initial pressures of about 10 mm., the constant being given by $\ln k = 26{\cdot}74 - 33{,}800/RT$.

H. J. Schumacher and G. Sprenger [86] have studied the thermal decomposition of nitryl chloride, $2NO_2Cl = 2NO_2 + Cl_2$, which they describe as a reaction of the first order. As far as the influence of pressure on the rate of change goes, it approximates much more closely to a reaction of the second order, since the influence of pressure on the unimolecular velocity constants even at 10 atmospheres shows no sign of diminishing (as it should in a quasi-unimolecular reaction). Moreover, the relation between the heat of activation and the absolute rate of change is more nearly characteristic of reactions of the bimolecular type. The heat of activation is 20,500 calories. Taking, for example, the experimental data for 140° and 506 mm., the number of molecules which would react in a simple bimolecular reaction with activation in

[82] F. F. Musgrave and C. N. Hinshelwood, *Proc. Roy. Soc.*, 1932, in the press.

[83] E. J. Bowen, E. A. Moelwyn-Hughes, and C. N. Hinshelwood, *ibid.*, 1931, [*A*], **134**, 211.

[84] R. L. Geddes and E. Mack, *J. Amer. Chem. Soc.*, 1930, **52**, 4372; *A.*, 1931, 78.

[85] H. C. Ramsperger and J. A. Leermakers, *ibid.*, 1931, **53**, 2061; *A.*, 916.

[86] *Z. physikal. Chem.*, 1931, [*B*], **12**, 115; *A.*, 1931, 915; *ibid.*, **13**, 267.

two squared terms only is about 5×10^{17}, while the actual number reacting is about $2{\cdot}3 \times 10^{16}$. Thus we are within about one power of ten of the theoretical number; this is more characteristic of the "bimolecular" region than of the "unimolecular" region.

The authors apparently prefer to call the reaction unimolecular, principally because the complete course of the change for a given initial concentration is adequately described by an equation of the first order. But it appears also that the products of reaction have a specific accelerating influence, so that this constancy of the unimolecular k must be largely accidental. Although this matter is really one of nomenclature, it is mentioned here because a good deal of confusion sometimes arises now about the use of the term "order of reaction" and some convention should perhaps be agreed on. As a result of complications due to catalysis by products and so on, the order deduced from the influence of the initial concentration is not always the same as that which gives the best equation to express the course of the reaction with time for a given initial pressure. This comes to light particularly clearly in the nitryl chloride reaction. It seems to the reviewer that the more significant order is that which describes the influence of changing pressure.

The slow decomposition of diazomethane [87] between 140° and 220° is stated to be bimolecular; probably over an extended range of pressures the order would also prove variable here. The thermal decomposition of methane, according to G. C. Holliday and W. J. Gooderham,[88] takes place in two stages in the first of which two molecules of methane react together to give C_2H_2. Interesting preliminary observations [89] on the reaction $Cl_2 + Br_2 = 2BrCl$ indicate that it may be a bimolecular reaction proceeding according to the simplest possible law, with a heat of activation of about 14,000 cals.

The observation [90] that the decomposition of nitrogen pentoxide ceases entirely below a certain pressure does not appear to be correct, though a definite falling off in the specific rate in the neighbourhood of 0·06 mm. now seems to be established,[91] in accordance with theoretical expectations. This reaction therefore is also of the quasi-unimolecular class.

[87] E. W. R. Steacie, *J. Physical Chem.*, 1931, **35**, 1493; *A.*, 916.
[88] *J.*, 1931, 1594; *A.*, 915.
[89] W. Jost, *Z. physikal. Chem.*, 1931, [*B*], **14**, 413.
[90] G. Sprenger, *ibid.*, 1928, **136**, 149; *A.*, 1928, 1099.
[91] H. C. Ramsperger and R. C. Tolman, *Proc. Nat. Acad. Sci.*, 1930, **16**, 6; *A.*, 1930, 547; H. J. Schumacher and G. Sprenger, *ibid.*, p. 129; *A.*, 1930, 708; J. H. Hibben, *J. Physical Chem.*, 1930, **34**, 1387; *A.*, 1930, 1127; J. H. Hodges and E. F. Linhorst, *Proc. Nat. Acad. Sci.*, 1931, **17**, 28; *A.*, 436.

If it turns out to be true that quite simple molecules such as N_2O can survive the activating collision and decompose spontaneously giving a free atom after a certain finite lapse of time, then the reverse process, namely, the combination of two simple structures such as atoms to give one molecule, becomes a thermodynamic necessity. In these circumstances the generally accepted principle that ternary collisions are necessary for combination between two atoms to occur loses its general validity. According to M. Volmer [92] the newly formed molecule may be in a state where the quantisation of vibrational energy is no longer sharply defined. If this is so the necessity of the ternary collision to allow the correct adjustment of the energy of the molecule formed to the quantum requirements no longer exists.

An interesting study has been made by G. B. Kistiakowsky and M. Nelles [93] of the slow isomerisation in the gas phase of dimethyl maleate into dimethyl fumarate, which occurs in the region of 300°. The reaction is of the quasi-unimolecular type, but unlike most reactions of this kind it shows an abnormally small rate, being only about 10^{-3} of that calculated on the assumption that two square terms are involved in the activation process. Thus, not only are the degrees of freedom of the molecules mostly inactive, but in addition a great many of the collisions are from the chemical point of view inelastic.

In the following will be briefly summarised a few results of outstanding importance in connexion with the mechanism of chemical reactions.

D. L. Chapman and F. B. Gibbs [94] have shown that if chlorine is sufficiently purified from oxygen it combines with hydrogen at a rate proportional to the square root of the light intensity. This is because the chlorine atoms propagating the reaction chains are removed by recombination rather than by the chemical action of foreign substances (as occurs in the incompletely purified gases). Thus the hydrogen–chlorine combinations falls into line with the corresponding bromine reaction, the rate of which is usually proportional to the square root of the intensity, but becomes proportional to the first power of the intensity in the presence of certain deliberately introduced impurities. In connexion with the well-known induction period in the hydrogen–chlorine reaction, shown long ago by Chapman to be due to the presence of nitrogen trichloride, it should be mentioned that the photosensitised decomposition of this latter substance has been studied by J. G. A. Griffiths

[92] *Z. physikal. Chem.*, 1931, [*B*], **13**, 299.
[93] *Ibid.*, 1931, Bodenstein Festband, p. 369; *A.*, 1239.
[94] *Nature*, 1931, **127**, 854; *A.*, 806.

and R. G. W. Norrish,[95] and correlated with the inhibition of the hydrogen–chlorine combination. M. Bodenstein and W. Unger [96] have discovered another mechanism by which the chains in the photochemical hydrogen chloride formation are broken, namely, a direct chemical reaction in the gas phase between some of the chain carriers and a gaseous silicon compound formed by the action of activated chlorine on the glass or silica walls of the vessel.

Franck and Bodenstein [97] have suggested the following modification of the Nernst chain in the combination of hydrogen and chlorine :

(1) $Cl_2 + h\nu = 2Cl$;
(2) $Cl + H_2O + H_2 = HCl + H_2O + H$;
(3) $H + Cl_2 + H_2 = 2HCl + H$;
(4) $H + O_2 + H_2 = H_2O + OH$;
(5) $H + O_2 + Cl_2 = HCl + ClO_2$.

For the rate of reaction this scheme gives the equation

$$\frac{d[HCl]}{dt} = \frac{2k_3I[Cl_2][H_2]}{[O_2](k_4[H_2] + k_5[Cl_2])}$$

which expresses adequately most of the experimental results (I is the intensity). The chief experimental reason for introducing the new hypothesis is the necessity for the presence of a small concentration of water vapour reported by Coehn and Jung. Thus step (2) is one of the simplest reactions which can follow (1) if a hydrogen atom is to be produced as in the original Nernst chain. The concentrations of steam molecules and chlorine atoms are, however, very minute, and if it be supposed that at each step in the cycle of changes a chlorine atom and a steam molecule must meet, there is the greatest difficulty in accounting for the observed rate of reaction. To avoid this difficulty, chlorine atoms are assigned no rôle except in the first link of the chain, the subsequent steps all depending on the reaction and re-formation of hydrogen atoms in the series of termolecular processes represented above. It is also interesting to note that the photochemical formation of hydrogen chloride takes place with an effective quantum yield when the light is absorbed in the band region of the chlorine spectrum,[98] *i.e.*, where activated molecules and not free atoms are

[95] *Nature*, 1931, **127**, 14; *Proc. Roy. Soc.*, 1931, [*A*], **130**, 591; *A.*, 179, 578.
[96] *Z. physikal. Chem.*, 1930, [*B*], **11**, 253; *A.*, 1931, 319.
[97] M. Bodenstein, Faraday Society, Liverpool Meeting, 1931; *Trans. Faraday Soc.*, 1931, **27**, 413; *A.*, 1136.
[98] E. Hertel, *Z. physikal. Chem.*, 1931, [*B*], **14**, 443.

primarily formed. These molecules are supposed to give atoms in subsequent collisions.

The following investigations illustrate interesting points of principle in connexion with the theory of chain reactions. H. W. Melville and E. B. Ludlam [99] have studied the influence of a long series of foreign gases on the lower critical limit encountered in the oxidation of phosphorus vapour, and have established a definite correlation between the influence of the gas and the diffusion coefficient through it of the chain-propagating molecules, thus confirming the view that at the critical limit the branching of the chains just ceases to be kept in check by deactivation at the wall of the vessel. In this connexion also reference may be made to an elaborate mathematical treatment [1] of chain reactions by the application of the classical diffusion equations.

A curious phenomenon shown by mixtures of hydrogen sulphide and oxygen has been observed by H. W. Thompson [2]: under appropriate conditions a series of successive explosions takes place, each being preceded by an increasing time lag. The effect seems to be connected with the formation of a catalytic substance during an induction period and the occurrence of an explosion when a critical limit is reached, the explosion being incomplete, however. During an ensuing induction period a critical concentration is again reached.

Norrish [3] has observed a sharp limiting pressure of chlorine in mixtures with hydrogen and oxygen above which an explosion occurs when the gases are exposed to the light of a mercury lamp at 300°.

In the last report reference [4] was made to the fact that atomic reactions of the type $Na + Cl_2 = NaCl + Cl$ may not always occur without activation, as the work of Polanyi and others on dilute alkali metal–halogen flames had suggested. The whole question has been dealt with in a paper by H. von Hartel and M. Polanyi,[5] who find that in the reactions between sodium vapour and the methyl halides the activation energy is nil for the iodide and rises regularly through the bromide and chloride to the fluoride. There is also an appreciable " inertia " associated with the reaction between sodium vapour and cyanogen, but since this is independent

[99] *Proc. Roy. Soc.*, 1931, [*A*], **132**, 108; *A.*, 1014.

[1] V. Bursian and V. Sorokin, *Z. physikal. Chem.*, 1931, [*B*], **12**, 247; *A.*, 688.

[2] *Nature*, 1931, **127**, 629; *A.*, 689; also H. W. Thompson and N. S. Kelland, *J.*, 1931, 1809; *A.*, 1014.

[3] *Nature*, 1931, **127**, 853; *A.*, 805.

[4] *Ann. Reports*, 1930, **27**, 20.

[5] *Z. physikal. Chem.*, 1930, *B*, **11**, 97; *A.*, 174.

of temperature it must depend upon some kind of "steric" factor rather than upon the necessity for activation. Although the principle that atomic reactions do not require activation ceases to be absolute, it remains true to say that many such reactions do proceed without activation, and also that the heat of activation of others is generally quite small.

C. N. HINSHELWOOD.

INORGANIC CHEMISTRY.

THERE has been a steady output of papers on Inorganic Chemistry during the past year but rather smaller in amount than for some years past. The discovery of the missing alkali metal—No. 87—by J. Papish has been announced,[1] but it is not possible at present to say whether the claim rests on any sound basis. Optically active compounds of nickel have been prepared which owe their activity to six-co-ordinated nickel.[2] Reports on all atomic-weight work in the previous year will in future be issued at the beginning of each year by the Committee on Atomic Weights of the International Union of Chemistry. This makes it unnecessary to consider atomic-weight determinations in the present Report. The first report on atomic weights under the new régime dealt with work published during 1930 and was issued in June.[3]

The other special topics which have been considered in the last two annual reports no longer seem to call for special mention, and any paper bearing upon them, to which it is desired to refer, will be mentioned under the group of elements most directly affected.

Group 0.

The transition temperature of the two forms of liquid helium is lowered as the pressure is increased.[4] Further details have been published of improved methods of extracting krypton and xenon from liquid-air residues, and of the redetermination of various constants.[5]

Group I.

It is becoming increasingly evident that the peculiar effects on the boiling of liquids produced by very complete removal of traces of moisture are due to superheating and not to a true elevation of boiling point brought about by some disturbance of the inner

[1] See note in *Nature*, 1931, **128**, 696 ; J. Papish and E. Wainer, *J. Amer. Chem. Soc.*, 1931, **53**, 3818 ; *A.*, 1348.

[2] G. T. Morgan and F. H. Burstall, *J.*, 1931, 2213; *A.*, 1168; *Nature*, 1931, **127**, 854; *A.*, 895.

[3] *J.*, 1931, 1617.

[4] W. H. Keesom and K. Clusius, *Proc. K. Akad. Wetensch. Amsterdam*, 1931, **34**, 605; *Naturwiss.*, 1931, **19**, 462; *A.*, 1004.

[5] F. J. Allen and R. B. Moore, *J. Amer. Chem. Soc.*, 1931, **53**, 2512, 2522; *A.*, 1117.

equilibrium of the liquid.[6] The direct formation of hydrogen peroxide from hydrogen and oxygen has been studied between 510° and 650° at pressures of 5—760 mm. and it has been shown to be a primary product.[7] The yield of hydrogen peroxide (and of ammonium persulphate) in the electrolytic method of preparation can be considerably increased by using a streaming electrolyte.[8] The displacement of arsenic, antimony, and bismuth from solutions of their salts by hydrogen under high pressure has been studied.[9]

No anhydrous polyiodide of potassium can exist at 25° or above,[10] but the hydrated compounds KI_3,H_2O and KI_7,H_2O, as well as the benzene compound $KI_7,2C_6H_6$, all exist at 25°.[11] The polybromides of cæsium are analogous to the polyiodides in so far as tri- and tetra-bromides exist but not a pentabromide.[12] Pure sodium monoxide may be prepared by heating sodium azide with sodium nitrite or nitrate in a nickel crucible. The reaction is smooth and easy to control but is not applicable to potassium monoxide. Reaction with oxygen to form peroxide is only slow at moderate temperatures, but at 100° nitric oxide reacts vigorously to form, among other products, sodium hyponitrite, which can be obtained in a very pure state by suitable treatment. Various decompositions of sodium hyponitrite have been studied.[13]

T. G. Pearson and P. L. Robinson have continued their work on polysulphides and have examined those of lithium, potassium, and rubidium.[14] Rubidium and cæsium metaplumbates [15] and hypophosphites [16] have been prepared. An account has been published of much further work on the curious salt-like compounds of sodium with certain heavy metals such as Na_4Sn_9 and Na_4Pb_9 which are

[6] E. Cohen and W. A. T. Cohen-de Meester, *Proc. K. Akad. Wetensch. Amsterdam*, 1930, **33**, 1003; *A.*, 1931, 294; A. Smits, E. L. Swart, P. Bruin, and W. M. Mazee, *Z. physikal. Chem.*, 1931, **153**, 255; *A.*, 430; J. W. Smith, *J.*, 1931, 2573.

[7] R. N. Pease, *J. Amer. Chem. Soc.*, 1930, **52**, 5106; *A.*, 320.

[8] E. H. Riesenfeld and A. Solovian, *Z. physikal. Chem.*, Bodenstein Festband, 1931, 405; *A.*, 1248.

[9] V. V. Ipatiev, jun., M. N. Platonova, and V. S. Malinovski, *Ber.*, 1931, **64**, [*B*], 1959; *A.*, 1242; V. V. Ipatiev, jun., and V. I. Tichomirov, *ibid.*, p. 1951; *A.*, 1242; V. V. Ipatiev, jun., I. R. Molkentin, and V. P. Theodorovitsch, *ibid.*, p. 1964; *A.*, 1243.

[10] *Ann. Reports*, 1930, **27**, 57; W. D. Bancroft, G. A. Scherer, and L. P. Gould, *J. Physical Chem.*, 1931, **35**, 764; *A.*, 580.

[11] N. S. Grace, *J.*, 1931, 594; *A.*, 580.

[12] N. Rae, *ibid.*, p. 1578; *A.*, 921.

[13] J. R. Partington and C. C. Shah, *ibid.*, p. 2071; *A.*, 1140.

[14] *Ibid.*, pp. 413, 1304, 1983; *A.*, 443, 807, 1139.

[15] E. R. Sbiera, *Bul. Fac. Stiinte Cernauti*, 1927, **1**, 59; *Chem. Zentr.*, 1931, i, 1262; *A.*, 1931, 808.

[16] L. Hackspill and J. Weiss, *Compt. rend.*, 1931, **192**, 425; *A.*, 443.

soluble in liquid ammonia in the form of ammines.[17] A number of interesting compounds of the alkali metals with salicylaldehyde have been prepared by F. M. Brewer,[18] who has by their help been able to establish the following covalency numbers: lithium 4; sodium 4; potassium, rubidium, and cæsium 4 and 6.

The dissociation pressures of the reaction $2CuCl_2 \rightleftharpoons 2CuCl + Cl_2$ have been measured between 360° and 500°.[19]

The existence of the compounds $Cu_2Cl_2,2CO$ and $Cu_2Br_2,2CO$ has been established by a study of the gas pressures during the action of carbon monoxide on cuprous chloride or bromide. The iodide probably yields a similar compound, but far more slowly. Similar silver and gold compounds could not be obtained.[20]

The products precipitated by the action of sulphite upon solutions of cupric selenite depend upon the p_H of the solution and may consist of cuprous oxide, cuprous or cupric selenide, or selenium. The conditions under which pure cuprous or cupric selenide can be obtained have been established.[21] Cupric perchlorate has been prepared as a hepta- and a di-hydrate, as well as a number of ammine derivatives.[22] The conductivities of the copper (zinc or nickel) salts of various alkyl-substituted malonic acids have been measured,[23] and potentiometric measurements have been made with the copper salts of various substituted aminoacetic acids.[24] Conclusions are drawn as to the effects of the substituents on complex-anion formation.

Silver hydride is a salt-like compound showing great analogy to lithium hydride. It can be obtained by prolonged action of atomic hydrogen on silver foil.[25] There are two modifications of silver iodide stable below 146°, one cubic (zinc blende type) and one hexagonal (wurtzite type). Another cubic variety is formed above 146°.[26] A number of well-crystallised salts of bivalent silver have been prepared in which the argentic ion has been stabilised in the first place by co-ordination with $\alpha\alpha'$-dipyridyl and secondly by

[17] E. Zintl, J. Goubeau, W. Dullenkopf, and A. Harder, *Z. physikal. Chem.*, 1931, **154**, 1, 47; *A.*, 695; *Ann. Reports*, 1929, **26**, 42.

[18] *J.*, 1931, 361; *A.*, 443.

[19] (Mlle.) A. E. Korvezee, *Rec. trav. chim.*, 1931, **50**, 505; *A.*, 684.

[20] O. H. Wagner, *Z. anorg. Chem.*, 1931, **196**, 364; *A.*, 581.

[21] W. Geilmann and F. W. Wrigge, *Z. anorg. Chem.*, 1931, **197**, 375; *A.*, 809.

[22] R. Portillo and L. Alberola, *Anal. Fis. Quim.*, 1930, **28**, 1117; R. Portillo, *ibid.*, p. 1125; *A.*, 1931, 49.

[23] D. J. G. Ives and H. L. Riley, *J.*, 1931, 1998; *A.*, 1126.

[24] H. L. Riley and V. Gallafent, *ibid.*, p. 2029; *A.*, 1126.

[25] E. Pietsch and F. Seuferling, *Naturwiss.*, 1931, **19**, 573; *A.*, 1019.

[26] R. Bloch and H. Möller, *Z. physikal. Chem.*, 1931, **152**, 245; *A.*, 444.

union with strongly oxidising anions such as the nitrate, chlorate, perchlorate, or persulphate ions.[27]

The superconductivity of gold–bismuth alloys has been shown to be due to the definite compound Au_2Bi.[28] Direct introduction of gold into the aromatic nucleus has been shown to be possible by the action of auric chloride on various aromatic compounds.[29] A large number of derivatives of auric bromide have been prepared [30] which show that probably auric gold always has a co-ordination number of four and that auric bromide itself is $(AuBr_3)_n$ where n is at least 2.

Group II.

A number of beryllium compounds have been prepared from the purified basic acetate, and their behaviour on electrolysis in a number of non-aqueous solvents has been examined. None of these solutions is suitable for the preparation of metallic beryllium.[31]

In corrosion experiments with magnesium and magnesium alloys, a mixture of chromic acid and silver chromate has been found useful for removing corrosion products.[32] Dehydration isotherms show that only monohydrates and octahydrates of strontium and barium hydroxides exist. It is doubtful whether calcium hydroxide forms any hydrate.[33] The peroxides of all three metals form octahydrates, however, which react as true peroxides, liberating iodine from neutral iodide solutions and not yielding free hydrogen peroxide when extracted with ether.[34] Several barium polysulphides have been isolated but individual calcium compounds could not be obtained.[35] Various equilibria involved in the formation of calcium cyanamide from calcium cyanide or carbide have been investigated.[36]

No evidence could be found for the various compounds of halogen acids with mercuric sulphate stated to exist by previous workers, but a compound $HgSO_4,HgI_2$ was obtained.[37] The preparation of $HgI_4[Zn(NH_3)_6]$ and of some similar compounds has been described.[38]

[27] G. T. Morgan and F. H. Burstall, *J.*, 1930, 2594; *A.*, 1931, 234.

[28] W. J. de Haas and F. Jurriaanse, *Naturwiss.*, 1931, **19**, 706; *A.*, 1224.

[29] M. S. Kharasch and H. S. Isbell, *J. Amer. Chem. Soc.*, 1931, **53**, 3053; *A.*, 1172.

[30] C. S. Gibson and W. M. Colles, *J.*, 1931, 2407; *A.*, 1316.

[31] H. S. Booth and G. G. Torrey, *J. Physical Chem.*, 1931, **35**, 2465, 2492; *A.*, 1249.

[32] L. Whitby, *J. Soc. Chem. Ind.*, 1931, **50**, 83T; *B.*, 544.

[33] C. Nogareda, *Anal. Fis. Quim.*, 1931, **29**, 33; *A.*, 412; G. F. Hüttig, A. Arbes, Z. Herrmann, and C. Slonim, *Z. anorg. Chem.*, 1931, **196**, 403; *A.*, 567.

[34] *Idem, ibid.*, p. 131; *A.*, 412.

[35] P. L. Robinson and W. E. Scott, *J.*, 1931, 693; *A.*, 695.

[36] A. Cochet, *Z. angew. Chem.*, 1931, **44**, 367; H. H. Franck and H. Heimann, *ibid.*, p. 372; *A.*, 807, 808.

[37] M. Paić, *Compt. rend.*, 1930, **191**, 941; *A.*, 1931, 50.

[38] M. E. Vojatsakis, *Bull. Soc. chim.*, 1931, [iv], **49**, 1029; *A.*, 1139.

Group III.

Solutions of B_2H_6 in liquid ammonia owe their electrolytic conductivity to the salt $B_2H_4,2NH_4$. The reactions which occur during the electrolysis of the solution at $-75°$ have been investigated.[39] The two principal reactions lead to the formation of $B_2H_4(NH_2)_2$ and of $B_2H_5 \cdot NH_2$.

Several forms of aluminium hydroxide exist, and attempts have been made to elucidate their relationships.[40] The precipitation of aluminium hydroxide has been followed conductometrically.[40a] By the addition of hydrogen peroxide to cold solutions of alkali aluminates, precipitates are obtained which are said to be peraluminates.[41]

Calcium and cadmium indates, CaO,In_2O_3 and CdO,In_2O_3, have been prepared by calcining at 900° nitrates mixed in the right proportion.[42]

The formation of a film of metal on the glass walls of the reaction tube during the reduction of thallous or lead chloride by hydrogen is attributed to the formation of volatile thallium or lead hydrides.[43] The reduction of thallic chloride by thiocyanate in aqueous solution has been examined.[44] Lanthanum and neodymium amalgams can be prepared by electrolysis of alcoholic chloride solutions with a mercury cathode.[44a] Details of a simplified method for extracting lanthanum from cerite with nitric acid have been published. Large quantities of material can be handled and a good product is said to be obtained.[45] Ceric selenate [46] and cerous sulphide [47] have been prepared, and a number of double sulphates and double selenates of neodymium have been examined.[48] Many anhydrous acetates and acid acetates of rare-earth metals have been reported,[49] as well as a number of complex ceric salts of organic acids.[50] Solubilities

[39] A. Stock, E. Wiberg, H. Martini, and A. Nicklas, *Z. physikal. Chem.*, Bodenstein Festband, 1931, 93; *A.*, 1248.

[40] V. Kohlschütter and W. Beutler, *Helv. Chim. Acta*, 1931, **14**, 305, 330; *A.*, 581; H. Kraut and H. Humme, *Ber.*, 1931, **64**, [*B*], 1697; *A.*, 1020.

[40a] R. A. Robinson and H. T. S. Britton, *J.*, 1931, 2817.

[41] J. Prášek, *Coll. Czech. Chem. Comm.*, 1930, **2**, 653; *A.*, 1931, 50.

[42] L. Passerini, *Gazzetta*, 1930, **60**, 754; *A.*, 1931, 151.

[43] E. Pietsch and F. Seuferling, *Naturwiss.*, 1931, **19**, 574; *A.*, 1020.

[44] I. K. Taimni, *J.*, 1931, 2433; *A.*, 1253.

[44a] L. F. Audrieth, E. E. Jukkola, R. E. Meints, and B. S. Hopkins, *J. Amer. Chem. Soc.*, 1931, **53**, 1805; *A.*, 805.

[45] R. Llord y Gamboa, *Anal. Fis. Quim.*, 1930, **28**, 1145; *A.*, 1931, 51.

[46] J. Meyer and F. Schulz, *Z. anorg. Chem.*, 1931, **195**, 127; *A.*, 323.

[47] Picon, *Compt. rend.*, 1931, **192**, 684; *A.*, 582.

[48] J. Meyer and (Frl.) C. Kittelmann, *Z. anorg. Chem.*, 1931, **195**, 121; *A.*, 321.

[49] A. Kotovski and H. Lehl, *ibid.*, **199**, 183; *A.*, 1020.

[50] L. Lortie, *Ann. Chim.*, 1930, [x], **14**, 407; *A.*, 1931, 182.

of lanthanum hydroxide and oxalate at 25° have been determined,[51] and also of neodymium selenates over the temperature range 0—100°.[52]

Group IV.

In the oxidation of methane by oxygen at 360° and 100 atmospheres pressure, as much as 17% of the methane burnt has been obtained as methyl alcohol, and 0·6% as formaldehyde with no trace of peroxide.[53] The reaction is over in a few minutes and it is concluded that the hydroxylation theory of combustion is still to be preferred to the peroxidation theory. A 17% yield of potassium oxalate can be obtained by the interaction of carbon dioxide with metallic potassium at 230—240°.[54]

Pure TiC, ZrC, HfC, NbC, and TaC have been prepared, and also TiN, ZrN, TaN, and the borides of the same metals. Details of the preparation and properties of the compounds are given.[55]

Disilicon hexafluoride, Si_2F_6, has been prepared by the interaction of the hexachloride with anhydrous zinc fluoride. It is instantly hydrolysed by moisture.[56] The formation of monosilicic acid and its polymerisation have been studied,[57] and a number of complex *cyclo*hexanol derivatives of silicic acids have been prepared by interaction of *cyclo*hexanol and silicon tetrachloride.[58]

Dehydration of hydrated stannous chloride by acetic anhydride is a convenient way of preparing the anhydrous compound.[59] Stannites and thio-oxystannites of calcium, strontium, and barium have been made by combination of stannous oxide or sulphide at high temperatures with the alkaline earth.[60]

There are only two polymorphic forms of lead monoxide, the red and the yellow. Black forms obtained from solution or by the action of heat or light on the red or the yellow form owe their colour to the presence of metallic lead.[61] Two types of lead dioxide are said to exist.[62]

[51] I. M. Kolthoff and (Miss) R. Elmquist, *J. Amer. Chem. Soc.*, 1931, **53**, 1217; *A.*, 677.

[52] J. A. N. Friend, *J.*, 1931, 1802; *A.*, 1020.

[53] W. A. Bone, *Nature*, 1931, **127**, 481; **128**, 188; *A.*, 598, 1030.

[54] M. Lemarchands and H. L. Roman, *Compt. rend.*, 1931, **192**, 1381; *A.*, 921.

[55] A. Agte, K. Moers, Heyne, and K. Becker, *Z. anorg. Chem.*, 1931, **198**, 233; *A.*, 921.

[56] W. C. Schumb and E. L. Gamble, *J. Amer. Chem. Soc.*, 1931, **53**, 3191; *A.*, 1140.

[57] H. Kraut, *Ber.*, 1931, **64**, [*B*], 1709; *A.*, 1021.

[58] R. Signer and H. Gross, *Annalen*, 1931, **488**, 56; *A.*, 1021.

[59] H. Stephen, *J.*, 1930, 2786; *A.*, 1931, 182.

[60] S. Tamaru and H. Sakurai, *Z. anorg. Chem.*, 1931, **195**, 24; S. Tamaru and Y. Tanaka, *ibid.*, p. 35; *A.*, 320, 321.

[61] M. P. Applebey and H. M. Powell, *J.*, 1931, 2821.

[62] E. J. Rode, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 1419; *A.*, 1931, 51.

The electrolytic formation of amalgams of titanium, uranium, and vanadium has been examined, and also some of the properties of the amalgams so obtained.[63] Cobalt and zinc orthotitanates have been prepared and added to the spinel group.[64] The extraction of germanium from germanite has been described.[65] Methods have been given for preparing germanic nitride,[66] sulphate, and oxychloride (Ge_2OCl_6),[67] and of a number of double compounds of germanium dichloride and tetrachloride with organic bases.[68] Work on germanium imide and germanomolybdic acid reported last year has been confirmed by other workers.[69]

Zirconium dibromide has been prepared as a black powder which reacts violently with water, liberating hydrogen. It is obtained at 350° by the reaction $2ZrBr_3 \longrightarrow ZrBr_4 + ZrBr_2$, whilst $ZrBr_3$ is prepared by reduction of $ZrBr_4$ with aluminium in an atmosphere of hydrogen at 450°. It is a bluish-black powder giving with water a rapidly fading yellow solution from which hydrogen is liberated and which has powerful reducing properties.[70] Normal zirconium oxalate can be precipitated from methyl-alcoholic solution, and also the aniline derivative $(PhN)_2Zr$.[71] Zirconium and hafnium sulphates are very difficult to prepare free from excess of sulphate.[72]

Group V.

The properties of nitrogen trifluoride have been examined and several intermediate stages in its formation have been isolated, including NH_2F and NHF_2 and a yellow compound which is thought to be NF_2. These are all gases at ordinary temperature and pressure.[73] Nitrogen tri-iodide also has been isolated by the action of dry ammonia on various iododibromides.[74]

The action of nitric oxide on alkaline hydroxides [75] and upon

[63] R. Groves and A. S. Russell, *J.*, 1931, 2805 ; *A.*, 1377.

[64] L. Passerini, *Gazzetta*, 1930, **60**, 957; *A.*, 1931, 289.

[65] W. I. Patnode and R. W. Work, *Ind. Eng. Chem.*, 1931, **23**, 204; *B.*, 495.

[66] W. C. Johnson, *J. Amer. Chem. Soc.*, 1930, **52**, 5160; *A.*, 1931, 322.

[67] R. Schwarz, P. W. Schenk, and H. Giese, *Ber.*, 1931, **64**, [*B*], 362; *A.*, 446.

[68] A. Tchakirian, *Compt. rend.*, 1931, **192**, 233; *A.*, 322; J. S. Thomas and W. W. Southwood, *J.*, 1931, 2083; *A.*, 1140.

[69] *Ann. Reports*, 1930, **27**, 65; J. S. Thomas and W. Pugh, *J.*, 1931, 60; C. G. Grosscup, *J. Amer. Chem. Soc.*, 1930, **52**, 5154; *A.*, 1931, 322.

[70] R. C. Young, *J. Amer. Chem. Soc.*, 1931, **53**, 2148; *A.*, 922.

[71] H. S. Gable, *ibid.*, 1931, **53**, 1276, 1612; *A.*, 696.

[72] G. von Hevesy and E. Cremer, *Z. anorg. Chem.*, 1931, **195**, 339; *A.*, 322.

[73] O. Ruff, W. Menzel, Hecht, E. Hanke, L. Staub, H. Wallauer, and E. Ascher, *ibid.*, **197**, 273; O. Ruff and E. Hanke, *ibid.*, p. 395; O. Ruff and (Frl.) L. Staub, *ibid.*, **198**, 32; *A.*, 696, 809.

[74] H. W. Cremer and D. R. Duncan, *J.*, 1930, 2750; *A.*, 1931, 182.

[75] E. Barnes, *J.*, 1931, 2605 ; *A.*, 1379.

various reducing agents [76] has been examined. Various reactions of $(HSN)_4$ have been studied, and the product obtained by the action of chlorine upon N_4S_4 is shown to have the formula $(NSCl)_3$ and is considered to be $N \lessdot \genfrac{}{}{0pt}{}{SCl:N}{SCl \cdot N} \gtrdot SCl$.[77] Variations in the density of red phosphorus dependent upon the temperature and pressure at which it has been produced from white phosphorus have been examined.[78]

Direct union of the elements yields phosphides and arsenides of niobium, tantalum, molybdenum, and tungsten,[79] and various phosphides result from the action of hypophosphites on acid or alkaline solutions of nickel or cobalt salts.[80]

The compounds $AlCl_3,PH_3$, $AlBr_3,PH_3$, and AlI_3,PH_3 are all readily formed and can be sublimed. Beryllium halides do not combine with phosphine.[81]

Addition compounds of phosphorus pentachloride and antimony pentachloride with pyridine have been reported.[82]

Nickel arsenide, Ni_3As_2, results from the prolonged action of finely divided nickel, reduced at a low temperature, upon a hot solution of arsenious chloride.[83]

Antimony bromodi-iodide, $SbBrI_2$, results from the action of bromine upon ethyldi-iodostibine, although chlorine yields only the tri-iodide.[84] *X*-Ray examination of the system bismuth–iodine shows that only the tri-iodide exists and no sub-iodide.[85] There are definite indications of the existence of a compound $Bi_2O_3,3H_2O$.[86]

A large number of internally complex organic acid salts of bismuth and of ter- and quinque-valent antimony and arsenic have been described.[87] From a study of the isomorphous relationships of its salts with those of several other metals, it is concluded that polonium

[76] H. Gehlen, *Ber.*, 1931, **64**, [*B*], 1267; M. L. Nichols and C. W. Morse, *J. Physical Chem.*, 1931, **35**, 1239; H. B. Dunnicliff, S. Mohammad, and J. Kishen, *ibid.*, p. 1721; *A.*, 922.

[77] A. Meuwsen and H. Holch, *Ber.*, 1931, **64**, [*B*], 2301; A. Meuwsen, *ibid.*, p. 2311; *A.*, 1254.

[78] V. N. Ipatiev, A. Frost, and A. V. Vedenski, *Bull. Soc. chim.*, 1931, [iv], **49**, 670; *A.*, 898.

[79] E. Heinerth and W. Biltz, *Z. anorg. Chem.*, 1931, **198**, 168; *A.*, 809.

[80] R. Scholder and H. Heckel, *ibid.*, p. 329; *A.*, 922.

[81] R. Höltze and F. Meyer, *ibid.*, **197**, 93; *A.*, 583.

[82] J. C. Hutton and H. W. Webb, *J.*, 1931, 1518; *A.*, 922.

[83] G. Arrivaut, *Compt. rend.*, 1931, **192**, 1238; *A.*, 810.

[84] R. E. D. Clark, *J.*, 1930, 2737; *A.*, 1931, 183.

[85] V. Caglioti, *Gazzetta*, 1930, **60**, 933; *A.*, 1931, 323.

[86] G. F. Hüttig, T. Tsugi, and B. Steiner, *Z. anorg. Chem.*, 1931, **200**, 74; *A.*, 1235.

[87] A. Rosenheim, I. Baruttschisky, W. Bulgrin, W. Plato, and G. Ebert, *ibid.*, p. 173; *A.*, 1254.

can have valencies of three and four.[88] An elaborate study has been made of the electrolytic reduction of vanadium through all the stages from quinque- to bi-valent, various kinds of electrodes being used.[89] The exact procedure in the electrolytic reduction of vanadic acid for the satisfactory isolation of crystalline vanadous sulphate heptahydrate has been worked out, and details given of the preparation of the relatively stable ammonium, potassium, and rubidium vanadous sulphates. Vanadous salts of other acids are less stable and are difficult to prepare.[90]

The interaction of niobium and tantalum pentoxides with the oxides of various metals has been studied in the solid state, and indications have been obtained of the formation of a number of new niobates and tantalates.[91] In an account of the isolation of protoactinium in the industrial treatment of pitchblende, it is shown that about 85% of the element present in the mineral dissolves with the uranium during the digestion with sulphuric acid. This was recovered by adsorption on a gel of tantalic acid.[92]

Group VI.

The formula $H_2S,6H_2O$ has been deduced for the hydrate of hydrogen sulphide.[93] It has been suggested that thiosulphonic acid is the primary product of the interaction of hydrogen sulphide and sulphur dioxide in presence of mercury and absence of water.[94] The effect of catalysts on the combination of sulphur monochloride with chlorine has been considered, as well as several peculiarities of the reaction.[95]

It has been shown that colloidal sulphur prepared from sodium thiosulphate is the sodium salt of a sulphur–polythionate complex, and that there is a definite equilibrium in the sol between the polythionate which is free and that which is bound, *i.e.*, attached to the complex. As the sol ages, more and more polythionate becomes free. The behaviour of the sol towards coagulants is quantitatively determined by the amount of bound polythionate.[96]

Selenium dioxide combines directly with hydrogen chloride or

[88] M. Guillot, *J. Chim. physique*, 1931, **28**, 92; *A.*, 697.

[89] F. Foerster and F. Böttcher, *Z. physikal. Chem.*, 1930, **151**, 321; *A.*, 1931, 178.

[90] J. Meyer and (Frl.) M. Aulich, *Z. anorg. Chem.*, 1930, **194**, 278; *A.*, 1931, 178.

[91] W. Jander and H. Frey, *ibid.*, 1931, **196**, 321; *A.*, 447.

[92] F. Reymond, *J. Chim. physique*, 1931, **28**, 409; *A.*, 1255.

[93] (Mlle.) A. Korvezee and F. E. C. Scheffer, *Rec. trav. chim.*, 1931, **50**, 256; *A.*, 583.

[94] B. S. Rao and M. R. A. Rao, *Nature*, 1931, **128**, 413; *A.*, 1134.

[95] T. M. Lowry and G. Jessop, *J.*, 1931, 323; *A.*, 438.

[96] H. Bassett and R. G. Durrant, *ibid.*, p. 2919.

bromide.[97] A number of complex selenocyanammines have been prepared.[98] Several papers have been published which deal with the passivity of chromium.[99]

A large number of very complex ammines of tervalent molybdenum have been described,[1] and so have complex cyanides and thiocyanates[2] of quadrivalent molybdenum and complex oxalates[3] and hydroxylamine[4] derivatives of sexavalent molybdenum. A number of complex molybdenum sulphates have also been investigated.[5]

Molybdenum-blue is considered to be $MoO_2,4MoO_3,xH_2O$.[6] Several oxy-salts (permolybdates) result from the action of hydrogen peroxide upon ammonium molybdate.[7] The precipitates formed by the interaction of sodium molybdates with various metal salts may consist of normal molybdate, basic molybdate, molybdic acid, or various mixtures, according to circumstances.[8] All the precipitates obtained by means of sodium tungstates are essentially basic in nature.[9] $5Na_2O,12WO_3,28H_2O$ was obtained by the action of formic acid upon sodium tungstate. Similar potassium and barium salts were also prepared.[10] Apparently W_2O_5 does not exist, and only WO_2 and W_4O_{11} of the lower oxides of tungsten are stable.[11] Several complex quinquevalent molybdenum salts of previously known types have been recorded.[12]

Group VII.

Improvements in detail of some importance in the preparation of fluorine have been recorded.[13] A number of the physical constants

[97] T. W. Parker and P. L. Robinson, *J.*, 1931, 1314; *A.*, 923.

[98] G. Spacu and C. G. Macarovici, *Bul. Soc. Stiinte Cluj*, 1930, **5**, 169; *Chem. Zentr.*, 1930, ii, 708; *A.*, 1931, 183.

[99] E. Müller and O. Essin, *Z. Elektrochem.*, 1930, **36**, 963; E. Müller and K. Schwabe, *ibid.*, 1931, **37**, 185; W. J. Müller, *ibid.*, p. 328; *A.*, 1931, 173, 571, 915.

[1] A. Rosenheim, G. Abel, and R. Levy, *Z. anorg. Chem.*, 1931, **197**, 189; *A.*, 697.

[2] G. A. Barbieri, *Atti R. Accad. Lincei*, 1930, [vi], **12**, 55; **13**, 375; *A.*, 183, 1255.

[3] H. M. Spittle and W. Wardlaw, *J.*, 1931, 1748; *A.*, 1035.

[4] W. F. Jakób and B. Jezowska, *Rocz. Chem.*, 1931, **11**, 229; *A.*, 923.

[5] F. H. Nicholls, H. Saenger, and W. Wardlaw, *J.*, 1931, 1443; *A.*, 923.

[6] C. R. Zinzadzé, *Bull. Soc. chim.*, 1931, [iv], **49**, 872; *A.*, 1021.

[7] V. Caglioti, *Gazzetta*, 1931, **61**, 257; *A.*, 923.

[8] H. T. S. Britton and W. L. German, *J.*, 1931, 1429; *A.*, 911.

[9] *Idem*, *ibid.*, p. 709; *A.*, 697.

[10] R. H. Vallance, *ibid.*, p. 1421; *A.*, 923.

[11] E. Tarján, *Naturwiss.*, 1931, **19**, 166; *A.*, 447; J. A. M. van Liempt, *Rec. trav. chim.*, 1931, **50**, 343; *A.*, 583.

[12] A. Paulssen von Beck, *Z. anorg. Chem.*, 1931, **196**, 85; *A.*, 447.

[13] L. M. Dennis, J. M. Veeder, and E. G. Rochow, *J. Amer. Chem. Soc.*, 1931, **53**, 3263; *A.*, 1248.

of fluorine monoxide have been measured, as well as its chemical behaviour towards numerous elements and compounds. It is without action on dry glass and is non-explosive, but, physiologically, it is more dangerous than fluorine.[14]

A rapid and economical method of preparing large quantities of iodine trichloride [15] has been described, and a number of new polyhalides have been prepared.[16] Solubilities and dissociation pressures of many of the latter have been measured, and it has been shown that stability of the anion is favoured by symmetry and by the presence of one, but not more than one, iodine atom.[17] Isobars of the thermal decomposition of iodic acid show that HI_3O_8 is formed at 70° and I_2O_5 at 200°. When heated in air, I_2O_5 begins to decompose at 275°.[18]

Observations made on the transformation of pink manganese sulphide into the green form do not altogether agree with those reported last year.[19] A phosphate of tervalent manganese, $NH_4H_2Mn^{III}(PO_4)_2$, has been recorded.[20] Conflicting views have been put forward as to the existence of definite hydrates of manganese dioxide.[21]

There has been great activity in connexion with rhenium since potassium per-rhenate became available commercially.[22] Much of the arc spectrum of rhenium has been mapped,[23] and many physical constants of the metal have been measured. The melting point of rhenium is very high, being 3440° ± 50° Abs.[24] The fusion diagram of the system tungsten–rhenium has been examined.[25] Much work

[14] O. Ruff and W. Menzel, *Z. anorg. Chem.*, 1931, **198**, 39; *A.*, 810.

[15] E. C. Truesdale and F. C. Beyer, *J. Amer. Chem. Soc.*, 1931, **53**, 164; *A.*, 324.

[16] H. W. Cremer and D. R. Duncan, *J.*, 1931, 1857; *A.*, 1022.

[17] *Idem, ibid.*, p. 2243; *A.*, 1235.

[18] E. Moles and A. Perez-Vitoria, *Z. physikal. Chem.*, Bodenstein Festband, 1931, 583; *A.*, 1225.

[19] *Ann. Reports*, 1930, **27**, 73; H. B. Weiser and W. O. Milligan, *J. Physical Chem.*, 1931, **35**, 2330; *A.*, 1140.

[20] A. Yakimach, *Compt. rend.*, 1931, **192**, 1652; *A.*, 1022.

[21] A. Simon and F. Feher, *Kolloid-Z.*, 1931, **54**, 49; *A.*, 306; W. Biltz and O. Rahlfs, *Nach. Ges. Wiss. Göttingen*, 1930, 189; *Chem. Zentr.*, 1931, i, 46; *A.*, 583.

[22] *Ann. Reports*, 1930, **27**, 73.

[23] H. Schober and J. Birke, *Naturwiss.*, 1931, **19**, 211; *A.*, 404; W. Meidinger, *Z. Physik*, 1931, **68**, 331; *A.*, 540; W. F. Meggers, *Bur. Stand. J. Res.*, 1931, **6**, 1027; *A.*, 993.

[24] C. Agte, H. Alterthum, K. Becker, G. Heyne, and K. Moers, *Naturwiss.*, 1931, **19**, 108; *Z. anorg. Chem.*, 1931, **196**, 129; *A.*, 288, 448; K. Moeller, *Naturwiss.*, 1931, **19**, 575; *A.*, 1001.

[25] K. Becker and K. Moers, *Metallwirt.*, 1930, **9**, 1063; *Chem. Zentr.*, 1931, i, 750; *A.*, 676.

on the analytical chemistry of the element has been published during the past year [26] and summaries of its chemistry and geochemistry have appeared.[27]

Rhenium tetrachloride and a number of rhenichlorides have been prepared.[28] Black ReO_2 and purplish-red Re_2O_5 can be obtained by suitable reduction methods from per-rhenic acid.[29] Copper, nickel, and cobalt per-rhenates and various ammines of these compounds have been described.[30] Re_2S_7 is precipitated from aqueous solutions of potassium per-rhenate by either hydrogen sulphide or sodium thiosulphate. On heating it yields ReS_2. The corresponding selenides were also prepared.[31] Thio-derivatives of per-rhenic acid have been recorded,[32] but it is doubtful whether they really exist.[33] Densities of solutions of per-rhenic acid have been measured [34] and so has the heat of formation of ReS_2.[35]

Group VIII.

The behaviour on heating of hydrated ferrous and ferric oxides has been described,[36] and also the reduction by hydrogen of ferric oxide.[37] Crystalline $Fe_2O_3,4H_2O$ has been obtained by slow hydrolysis of a boiling dilute solution of ferric ethoxide in absolute alcohol.[38]

A number of reactions of the iron carbonyls have been described, including the formation of $Fe(CO)_4H_2$, which is a volatile yellow oil, by the action of bases on iron pentacarbonyl.[39] Further experiments with iron nitrosyls are described which are considered to

[26] C. Agte *et al.*, *Z. anorg. Chem.*, 1931, **196**, 129; *A.*, 448; F. Krauss and H. Steinfeld, *ibid.*, **197**, 52; *A.*, 589; W. Geilmann, F. Weibke, F. W. Wrigge, and K. Brünger, *ibid.*, **195**, 289; **199**, 65, 77, 120, 347; *A.*, 328, 1025, 1143.

[27] I. and W. Noddack, *Z. angew. Chem.*, 1931, **44**, 215; *Z. physikal. Chem.*, 1931, **154**, 207; *A.*, 583, 707.

[28] E. Enk, *Ber.*, 1931, **64**, [*B*], 791; *A.*, 810; H. V. A. Briscoe, P. L. Robinson, and E. M. Stoddart, *J.*, 1931, 2263; *A.*, 1255.

[29] *Idem*, *ibid.*, p. 666; *A.*, 584; H. V. A. Briscoe, P. L. Robinson, and A. J. Rudge, *ibid.*, p. 3087.

[30] *Idem*, *ibid.*, p. 2211; *A.*, 1139.

[31] H. V. A. Briscoe, P. L. Robinson, and E. M. Stoddart, *ibid.*, p. 1439; *A.*, 924.

[32] W. Feit, *Z. angew. Chem.*, 1931, **44**, 65; *Z. anorg. Chem.*, 1931, **199**, 263; *A.*, 924, 1255.

[33] H. V. A. Briscoe, P. L. Robinson, and E. M. Stoddart, *J.*, 1931, 2976.

[34] W. Feit, *Z. anorg. Chem.*, 1931, **199**, 271; *A.*, 1223.

[35] I. R. Juza and W. Biltz, *Z. Elektrochem.*, 1931, **37**, 498; *A.*, 1128.

[36] G. F. Hüttig and H. Möldner, *Z. anorg. Chem.*, 1931, **196**, 177; *A.*, 432; E. J. Rode, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 1443; *A.*, 1931, 53.

[37] E. J. Rode, *ibid.*, p. 1453; *A.*, 1931, 53.

[38] R. A. Thiessen and R. Köppen, *Z. anorg. Chem.*, 1931, **200**, 18; *A.*, 1255.

[39] W. Hieber and F. Leutert, *Naturwiss.*, 1931, **19**, 360; *A.*, 810; W. Hieber and H. Vetter, *Ber.*, 1931, **64**, [*B*], 2340; *A.* 1255.

oppose the view that certain of them—such as $Fe(S{\cdot}CS{\cdot}OEt)_2(NO)_2$ —contain univalent iron.[40] The red colour of the alkali ferrithiocyanates and of ferric thiocyanate itself is attributed to the ion $Fe(CNS)_6'''$ and the molecular weight of ferric thiocyanate in benzene and ether is found to correspond with the formula $Fe[Fe(CNS)_6]$.[41] Ilmenite and ferrous orthotitanate have been prepared by heating together at 900° suitable mixtures of titanium dioxide and ferrous oxalate. Ferric orthotitanate was similarly prepared, the individuality of the three compounds being confirmed by an *X*-ray analysis.[42]

Persulphatopentamminocobaltic sulphate, formulated as $[Co(SO_4)^{I}(NH_3)_5](SO_4)^{II},H_2O$, has been prepared, and the conclusion has been drawn that persulphuric acid is HSO_4 and not $H_2S_2O_8$.[43] Several tetramminocobaltic complexes containing thiosulphate are said to have been obtained.[44]

Various nickel dimethylglyoxime salts and related compounds have been prepared in an endeavour to find an explanation of the different behaviour of bivalent cobalt, nickel, and copper towards dimethylglyoxime. The main difference is attributed to the tendency of nickel to remain co-ordinatively quadrivalent while cobalt tends to be co-ordinatively sexavalent.[45]

A number of tris-αα′-dipyridyl nickelous salts have been prepared, and the resolution of the chloride has been effected with the help of ammonium *d*-tartrate. The active forms are rapidly racemised in aqueous solutions.[46] The effect of the temperature to which it has been heated on the solubility of nickel oxide in sulphuric acid has been examined in connexion with the extraction of copper oxide from roasted nickel–copper matte.[47]

The arsenides $RuAs_2$, $RhAs_2$, $PdAs_2$, $IrAs_2$, and $PtAs_2$ were prepared by heating a mixture of the chloride with excess of arsenic in a current of hydrogen.[48]

A number of complex derivatives of tervalent ruthenium [49] and

[40] H. Reihlen, E. Elben, and J. Everet, *Annalen*, 1931, **485**, 43; *A.*, 449.

[41] H. I. Schlesinger and H. B. Van Valkenburgh, *J. Amer. Chem. Soc.*, 1931, **53**, 1212; *A.*, 670.

[42] B. Pesce, *Gazzetta*, 1931, **61**, 107; *A.*, 584.

[43] C. Duval and (Mme.) Duval, *Compt. rend.*, 1930, **191**, 843; *A.*, 1931, 53.

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[48] L. Wöhler and R. F. A. Ewald, *Z. anorg. Chem.*, 1931, **199**, 57; *A.*, 1022.

[49] R. Charonnat, *Compt. rend.*, 1930, **191**, 1453; *A.*, 1931, 184; *Ann. Chim.*, 1931, [x], **16**, 5; *A.*, 1256.

rhodium [50] have been reported in all of which the ruthenium and rhodium have a co-ordination number of six. The action of various oxidising agents on OsS_4 has been examined.[51] The optical activities of a number of tetrammine salts of bivalent platinum and palladium show that the four linkings cannot lie in a plane.[52] On the other hand, Werner's views as to the structures of the two forms of $Pt(NH_3)_2Cl_2$ are supposed to be confirmed by the behaviour of the two compounds with oxalic acid.[53]

By the interaction of very dilute solutions of disodium hydrogen phosphate and ammonium chloroplatinate at room temperature, the compounds

$[Pt(NH_3)_4Cl(NH_2)](H_2PO_4)_2$ and $[Pt(NH_3)_4Cl(NH_2)](H_2PO_4)OH$

are formed. This has some bearing on the accurate analysis of some types of silicates, for there is a possibility of the above platinum compounds, formed from platinum dissolved from the apparatus, being precipitated with magnesium ammonium phosphate.[54]

Definite equilibria of the type, $PtBr_6'' + 6Cl' \rightleftharpoons PtCl_6'' + 6Br'$, exist and light accelerates attainment of equilibrium in aqueous solution. The concentration of chloride ion must be 660 times that of bromide ion for the equilibrium to be shifted 99% from left to right, while the concentration of bromide ion must be 25×10^3 that of iodide ion to cause a like shift in the reaction $PtI_6'' + 6Br' \rightleftharpoons PtBr_6'' + 6I'$. These figures indicate the relative order in which the halogen ions tend to co-ordinate with platinum.[55]

Systems and Equilibria.

Co–Cr [56]; Cr_2O_3–SiO_2 [57]; $NaI + KCl \longrightarrow KI + NaCl$ [58]; $NaNO_3$–Na_2SO_4–$MgCl_2$–H_2O [59]; strontium amalgams [60]; Fe–P–Si [61]; $Th(NO_3)_4$–Et_2O–H_2O [62]; $UO_2(NO_3)_2$–Et_2O–H_2O [63]; Li_2O–

[50] G. A. Barbieri, *Atti R. Accad. Lincei*, 1931, [vi], **13**, 433; *A.*, 1141.

[51] E. Fritzmann and E. M. Zuhn, *Z. anorg. Chem.*, 1931, **199**, 374; *A.*, 1141.

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[57] E. N. Bunting, *Bur. Stand. J. Res.*, 1930, **5**, 325; *A.*, 1931, 41.

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[63] *Idem, ibid.*, p. 839; *A.*, 1931, 160.

SiO_2 [64]; $HgCl_2(HgBr_2)$–$HgSO_4$ [65]; carbides of high m. p.[66]; Na_2SiO_3–Fe_2O_3–SiO_2 [67]; $[Co(NH_3)_5Cl]Cl_2 + 2HBr \rightleftarrows [Co(NH_3)_5Cl]Br_2 + 2HCl$ [68]; Li–Cu [69]; Bi–Se [70]; Al–Mn; Cu–Mn; Fe–Mn [71]; CaO–SiO_2–H_2O [72]; MgO–FeO–Fe_2O_3 [73]; KNO_3–$Ca(NO_3)_2$–H_2O [74]; $(NH_4)_2SO_4$–$MnSO_4$–H_2O, Tl_2SO_4–$MnSO_4$–H_2O, Rb_2SO_4–$MnSO_4$–H_2O [75]; $Ba(CNS)_2$–$NaCNS$–H_2O and $Ba(CNS)_2$–$KCNS$–H_2O [76]; Fe–C–Si [77]; Li–Ag [78]; I_2–H_2O [79]; ZrO_2–BeO [80]; KNO_3–$Ca(NO_3)_2$ [81]; $RbNO_3$–$RbCl$ [82]; $NaHCO_3$–Na_2SO_4–H_2O [83]; Cd–Ag [84]; $NaNO_3$–$NaIO_3$–H_2O [85]; $Mg(IO_3)_2$–$Mg(NO_3)_2$–H_2O [86]; $Ag_2SO_4 + Tl_2Cl_2 \rightleftarrows Tl_2SO_4 + Ag_2Cl_2$[87]; W–Re [88]; $CoCl_2$–$Co(NO_3)_2$–H_2O [89]; $(CH_2)_6N_4$–$MgCl_2(CaCl_2)$–H_2O [90]; $KCNS$–$Hg(CNS)_2$–H_2O [91]; $MgSO_4 + 2KNO_3 \rightleftarrows Mg(NO_3)_2 + K_2SO_4$ [91a];

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ORGANIC CHEMISTRY.

PART I.—ALIPHATIC DIVISION.

Olefinic and Polyolefinic Additions.

Mono-olefins.—The work of the past few years on the subject of olefinic and polyolefinic addition has increasingly focused attention on the following features of the addition process: (1) the polarised state of the olefin molecule, (2) the condition and manner in which the addendum enters reaction, (3) the point of attack in the olefinic chain (C_α, C_β, etc.), (4) the influence of substituents on the course and speed of reaction and (5) the influence of reaction conditions (temperature, solvent, catalytic action, etc.). All of these enter into consideration in connexion with orientation problems.

How profound are the effects of catalytic action on the orientation of addition products is to be gathered from the elaborate experiments of J. P. Wibaut and his collaborators [1] on the addition of gaseous hydrogen bromide to gaseous vinyl bromide in the presence of glass wool, asbestos and of metallic bromides. In these experiments the proportion of the isomeric dibromoethanes formed in the reaction varied extensively with changes in the chemical composition and physical condition of the catalyst, and quite frequently without assignable cause. The proportion also varied with the temperature of interaction, but there was no interconversion of the isomerides themselves when heated alone, or in the presence of catalysts. Similar experiments with acetylene and hydrogen bromide indicated that the primary formation of vinyl bromide takes place with greater difficulty than its subsequent conversion into dibromoethanes.

It has been shown by the same workers and independently by G. N. Burkhardt and W. Cocker [2] that the interaction of vinyl bromide with solutions of hydrogen bromide is very sensitive to changes of temperature, concentration and solvent, and apparently to some extent of illumination. It is suggested by the latter authors that for reactions in which the molecular activations are practically exclusively thermal, the reactivity of vinyl bromide towards the less concentrated aqueous solutions of hydrogen bromide can be represented schematically by $CH_2{=}CH{-}Br$, in which the existence

[1] *Rec. trav. chim.*, 1931, **50**, 313; *A.*, 598. [2] *Ibid.*, p. 837; *A.*, 1031.

of a "conjugative" effect[3] activating the β-positions for interaction with hydrion, and a "general" effect[3] minimising the effectiveness of these polarisations, is indicated. A large fraction of the general effect is considered to be transmitted by paths immediately outside the molecule, in which circumstances it would be especially sensitive to changes in the conditions external to the molecule such as would arise from changes of solvent and temperature. This effect would be most important near a halogen atom. The addition in question is a reaction which is characteristic of the ethylene bond itself; an atom or group immediately adjacent to a double bond would affect such a reaction by enhancing or suppressing, in some degree, one or other of the two opposite polarisations which are possible in the ethylene bond. This would give a mixed product unless the polarising group had a powerful effect. On the other hand, a property which is not shown by the ethylene bond, *e.g.*, addition of cyanide ion to kationoid carbon, would show itself at the carbon atom more remote from the polarising group and a single product would be expected if the reaction proceeded at all (compare the formation of ethylenediamine by the action of ammonia on vinyl chloride).[4] Quite other considerations would enter into the discussion of orientation in additions promoted by light and by surface action: the chemical composition of catalytic surfaces may exert an influence on the steric positions taken up by molecules in the adsorption layer ("directed adsorption"), but a more important influence than this in determining the orientation of addition products is probably the electronic distortion of the unsaturated system which takes place in the process of adsorption.

A more comprehensive hypothesis relating to the influence of substituents on the orientation of olefin addition products has been advanced by C. K. Ingold and E. H. Ingold:[5] in this the orientation principles developed in connexion with aromatic substitution and tautomeric phenomena are applied with suitable modification to additive processes. It is pointed out that when $\overset{\curvearrowleft}{X}$—Y adds to R—$C_\alpha \overset{\curvearrowright}{=} C_\beta$, the process being initiated by the orientation of ($\delta +$)Y to ($\delta -$)C_β (addition of Br_2, HBr, etc.),[6] the electron-

[3] Compare J. Allan, A. E. Oxford, R. Robinson, and J. C. Smith, *J.*, 1926, 404; *A.*, 1926, 397; A. Lapworth and R. Robinson, *Mem. Manchester Phil. Soc.*, 1927, **72**, 43.

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[5] *J.*, 1931, 2354; *A.*, 1267.

[6] It is admitted by the authors that addition initiated by the attack of ($\delta -$) Hal. would also be theoretically possible, provided that the intrinsically small reactivity of negative halogen could be overcome by the attachment

demand made on R might have any value between a very small one and that which corresponds to the development of a free integral charge on C_α; the actual value in a given case will depend on that degree of electrostriction between X and C_α which is necessary to determine the consolidation of the initial union between Y and C_β, or, in other words, on the degree to which the second stage of addition " backs up " and overlaps the first. This in turn depends, *inter alia*, on the degree of prior polarisation of X—Y, and the case of maximal electron-demand will arise in the addition of previously formed or dissociated ions.

The majority of those groups which activate anionotropic systems and promote aromatic hydrogen-replacement by ordinary substituting reagents will increase the additivity of an ethylene towards reagents such as halogens, halogen halides, and nitrogen peroxide, the more active ions of which are positive, and will decrease reactivity to such addenda as hydrogen, hydrogen cyanide, nitromethane, and ethyl malonate, whose more active ions are negative; and similarly most of those substituents which facilitate prototropy and aromatic halogen-replacement by basic reagents will deactivate the ethylene nucleus towards the former group of reagents and activate it towards the latter. It is recognised, however, that there are strongly restrictive limits to the validity of this reasoning.

It should be borne in mind that when two groups are attached to an ethenoid centre, the separate groups may not compound simply. For example, if de-activation results when two substituents are present, it does not necessarily follow that either would act in this sense if present singly. Furthermore it is not dissymmetric substitution and the consequent electrical dissymmetry of the double linking which constitute the primary influence of substitution; for the electron-displacements of the addition process must be substantially confined to the ethenoid centre and hence it is the polarisability of the corresponding electrons, not their state of polarisation, which is the important factor.

The classes of substituent for which distinctive effects on speeds of addition are expected to arise either when the constituent is the only one attached to the ethylenic centre, or when it is present in conjunction with other like or unlike groups, are symbolised as follows :

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of a sufficiently powerful electron-sink to the olefinic residue. It is not yet known whether any of the available groups (·CHO, ·COR, $\cdot NO_2$) are in fact competent to cause this anticipated reversal of normal reactivity; the practical criterion which would reveal such an occurrence would be that the rate of addition would pass through a minimum as the efficacy of the electron-sink was progressively increased.

Class	(1) $+I$	(2) $-I$	(3) $-I-T$	(4) $-I+T$
Example ...	$:C\leftarrow Me$	$:C\rightarrow NMe_3^{\oplus}$	$:C\rightarrow CO_2H$	$:C\rightarrow Br$
Class	(5) $+I+T$	(6) $+I-T$	(7) $\pm T$	
Example ...	$:C\leftarrow O^{\ominus}$	$:C\leftarrow CO_2^{\ominus}$	$:C$—Ph	

The methyl group (Class 1) repels electrons and should therefore facilitate the addition of a reagent such as bromine, the reactive ion of which is positive.

$$Me\rightarrow CH\!=\!\!=\!CH_2^{(\delta-)} \cdots\cdots\cdots\cdots \overset{(\delta+)}{Br}\text{—}\overset{(\delta-)}{Br}$$

The accumulation of methyl groups should (in the absence of groups possessing a mechanism for electromeric change) produce, and indeed has been shown in the case of alkylethylenes to produce, a progressive increase in the speed of addition. The carboxyl group (Class 3), the $-T$ effect of which is weak, either alone or in the presence of a substituent of Class 1 or 2, should invariably de-activate: this has been illustrated for acrylic and crotonic acids. With respect to the action of substituents of Class 4 it cannot be decided *a priori* whether the activating $+T$ will fail to compensate, or will over-compensate, the de-activating $-I$ effect; in vinyl bromide it is shown experimentally that the bromine substituent definitely de-activates and it is to be expected that any dibromoethylene and tetrabromoethylene will exhibit strong passivity. The phenyl group, like bromine, exhibits duplex polar action ($\pm T$) but with the difference that *both* the component effects are polarisabilities: of the two electromeric effects, it is the one symbolised by $+T$ which electron-demanding reaction should stimulate, wherefore the phenyl group should be an activator. The relative rates of bromine addition to styrene and ethylene show that this is the case, and the well-known passivity of tetraphenylethylene, and of certain other stilbene derivatives, is probably quite wrongly attributed to de-activation by phenyl groups.

The orienting influence of solvents is traced by C. K. Ingold and (Miss) E. Ramsden [7] to that portion of the effect of a polarising group which is transmitted *outside* the molecule itself: the latter in travelling through the medium is profoundly affected by the nature of the medium. For additions to $R\cdot CH\!:\!CH_2$, where R is an alkyl group, the externally propagated orienting influence is considered to repel electrons, anions, and the negative ends of polarised molecules, and to attract protons, kations, and the positive ends of polarised molecules. This effect must tend to orientate the adden-

[7] *J.*, 1931, 2746; *A.*, 1391.

dum in the sense of the expression R·CH(H)·CH_2(X). Certain aspects of the problem relating to the comparison of the orienting influence of solvents are discussed by the same authors. In connexion with the orienting influence of media, the statement that the composition of the product obtained by addition of hydrogen bromide to allyl bromide in glacial acetic acid is greatly changed when the reaction is carried out in a magnetic field is of interest.[8]

Information with regard to the location in the olefinic system of the point of initial attack does not emerge from a knowledge of the constitution of the addition products. The case of the halogens is, however, amenable to practical treatment on the assumption that the positive end of the halogen molecule initiates reaction : thus for addition of ICl, the location of the iodine atom in the addition product indicates the point of initiation of addition, and in tests carried out with propylene, styrene, and crotonic acid the results are found to be in accordance with the foregoing considerations concerning the directive influence of substituents.[9]

A useful review of the literature referring to the formation of ethylene chlorohydrin is contributed by E. D. G. Frahm.[10] This author appraises the efficiency of the various practical expedients which have been adopted for improving the yield of chlorohydrin and depressing that of dichloride formed according to the scheme :

$$C_2H_4Cl_2 \longleftarrow H_2O + Cl_2 \rightleftharpoons H^{\cdot} + Cl' + HOCl \longrightarrow C_2H_4(OH)Cl.$$

Acceleration of chlorohydrin formation and diminution of dichloride production were found to result from the catalytic action of certain metallic salts and it is suggested that chlorohydrin formation from ethylene and chlorine in aqueous media takes place by way of ethylene oxide. The degree of hydration of ethylene and propylene produced by heating with hydrochloric, hydrobromic, or hydriodic acid, or with aqueous solutions of various chlorides or of silver nitrate, at 100—200° does not exceed 0·6% even at a pressure of 800 lb. per sq. in.; high pressures, and temperatures of 227—427°, are reported to favour hydration.[11]

It is remarkable that β-chlorocrotonic acid and its sodium salt rapidly undergo catalytic reduction, although β-chlorobutyric acid does not.[11a] The reduction proceeds in stages—rapidly to

[8] R. H. Clarke and K. R. Gray, *Trans. Roy. Soc. Canada*, 1930, [iii], 24, III, 111; *A.*, 1931, 598; see also R. H. Clarke and E. G. Hallonquist, *ibid.*, p. 115; *A.*, 1931, 597.

[9] C. K. Ingold and H. G. Smith, *J.*, 1931, 2742; *A.*, 1391.

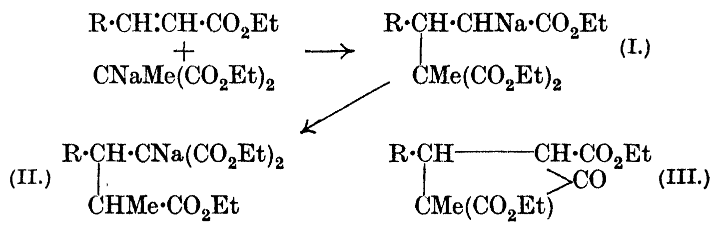
[10] *Rec. trav. chim.*, 1931, **50**, 261; *A.*, 598.

[11] R. D. Snow and D. B. Keyes, *Ind. Eng. Chem.*, 1930, **22**, 1048; *A.*, 1552; A. V. Frost, *J. Appl. Chem. Russia*, 1930, **3**, 1069; *A.*, 1931, 1267.

[11a] C. Paal, H. Schiedewitz, and K. Rauscher, *Ber.*, 1931, **64**, [*B*], 1521; *A.*, 934.

crotonic acid and then more slowly to butyric acid. The difference in rate of hydrogenation between chlorocrotonic and chloro*iso*crotonic acids serves to confirm the *cis-trans* nature of the isomerism existing between these acids.

The conclusions recently reached by A. Michael and J. Ross [12] with respect to the manner in which alkylated malonic and cyanoacetic esters divide when acting as addenda in the Michael reaction are considered by N. E. Holden and A. Lapworth [13] to be erroneous. The latter authors suggest, and bring evidence in support of the view, that the *apparently* realisable partition of an alkylated sodio-ester such as ethyl sodiomethylmalonate in the manner CH_3—¦—$CNa(CO_2Et)_2$ instead of Na—¦—$CMe(CO_2Et)_2$ results from an interchange (in effect) of ·CO_2Et (·CN for an alkylated cyano-ester) for the H of the ·CHNa group in the normal addition product. Thus in additions to αβ-unsaturated esters of the general type R·CH:CH·CO_2Et the normal addition product (I) may suffer extensive change to the isomeric compound (II) either intramolecularly (*e.g.*, *via* the sodio-derivative of the Dieckmann product III) or by an intermolecular process.[14] The occurrence of such a change under the conditions utilised by Michael and Ross (*i.e.*, the employment of a whole molecular proportion of sodium ethoxide for effecting condensation) is not inconsistent with already known reactivities.



In connexion with the characterisation of conjugated butadienes by the formation of crystalline addition products with maleic anhydride, certain olefins (*e.g.*, styrene and indene) have been shown to yield non-crystalline polymolecular addition products with the same reagent; in one case (*as*-diphenylethylene), however, a relatively simple, although rather high-melting, *crystalline* addition product has been obtained and there appears to be need for the exercise of care in applying the Diels–Alder reaction to the diagnosis of conjugated unsaturation.[15]

[12] *J. Amer. Chem. Soc.*, 1930, **52**, 4598; 1931, **53**, 1150; *A.*, 1931, 67; 603.

[13] *J.*, 1931, 2370; *A.*, 1272.

[14] The transformations are represented for convenience in terms of conventionally formulated sodio-derivatives.

[15] T. Wagner-Jauregg, *Ber.*, 1930, **63**, [*B*], 3213; *A.*, 1931, 198; *Annalen*, 1931, **491**, 1.

Polyolefins.—A notable synthesis of an open-chain poly-ene has been achieved by P. Karrer and A. Helfenstein in producing a hydrocarbon containing squalene from farnesyl bromide.[16] The conversion is brought about in ethereal solution by the action of potassium or activated magnesium, and the product yields the crystalline hexahydrochloride described by I. M. Heilbron, E. D. Kamm, and W. M. Owen.[17] Squalene is therefore correctly represented by the formula

$$(CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot})_2.$$

Recognition that the crystalline additive compound of isoprene with sulphur dioxide is a cyclic sulphone has been followed by the production of an isomeric compound by the action of ultra-violet light on a solution of the first compound.[18] The double bond appears to be retained in the original position and the possibility that the cause of isomerism resides in the sulphone group is rejected on chemical grounds. The two substances yield the same dihydro-derivative and are considered to display *cis-* and *trans-* attachments respectively of the $\cdot CH_2{\cdot}SO_2{\cdot}CH_2\cdot$ chain to the terminals of the ethylenic bond, so giving planar and pleated ring configurations.

An important point affecting the classification of additive reactions in the conjugated poly-ene series turns on the mechanism of the Michael reaction. If in this reaction the addendum attacks by means of its anion, as in hydrogen cyanide additions,[19] then it must be assumed that any polarisations of the unsaturated molecule which are capable of influencing the additive mode must exist *before* the anion enters the unsaturated molecule; moreover, any plurality of addition products in a given instance must be explained by assuming different polarisations of the butadienoid molecule, leading to the production of isomeric anions such as A and B, which are only interconvertible *via* the retrograde Michael reaction (αδ-product ⇌ reactants ⇌ αβ-product).

(A) $Me{\cdot}CH{\cdot}\overset{\ominus}{C}H{\cdot}CH{:}CH{\cdot}CO_2Et$, with $CH(CO_2Et)_2$ attached to the first CH
(capable of prototropic change)

(B) $Me{\cdot}CH{:}CH{\cdot}CH{\cdot}\overset{\ominus}{C}H{\cdot}CO_2Et$, with $CH(CO_2Et)_2$ attached to the third CH
(non-tautomeric)

This is necessarily the case, since the prospect of attachment of the addendum at the δ-carbon atom would be non-existent were it not for the presence of a group such as carbonyl in the molecule (in other words, the addendum in the Michael reaction is not an additive

16 *Helv. Chim. Acta*, 1931, **14**, 78; *A.*, 333.

17 *J.*, 1926, 1630; *A.*, 1926, 816.

18 E. Eigenburger, *J. pr. Chem.*, 1931, [ii], **129**, 312; **131**, 289; *A.*, 600, 1268.

19 A. Lapworth, *J.*, 1903, **83**, 995; 1904, **85**, 1206.

reagent for purely ethylenic centres); therefore, granting successful attack by the anion of the reagent, it follows that the influence of the activating group (carbonyl) is felt, and is effective in promoting reaction, at the δ-carbon atom—that is to say, a state of conjugation is effectively established or induced in the poly-ene chain.

It has been found by E. H. Farmer and T. N. Mehta [20] that the ratios in which αβ- and αδ-ester-addition products are formed from the members of a series of alkyl-substituted butadiene-α-carboxylic esters are not those to be expected on the basis of an anionotropically controlled incidence of addition products. Taking sorbic ester as the standard, it is seen from the figures quoted that (*a*) deprivation

	αβ (%).		αβ (%).
$CH_3\cdot CH{:}CH\cdot CH{:}CHX$ (sorbic ester)	7—10	$CH_3\cdot CH{:}CH\cdot CH{:}CX_2$	no addition
$CH_2{:}CH\cdot CH{:}CHX$	<2*	$CH_3\cdot CH{:}CMe\cdot CH{:}CHX$	70—74·5
$CH_3\cdot CH{:}CH\cdot CMe{:}CHX$	<7	$CH_3\cdot CH{:}CH\cdot CH{:}CHAc$	27—29
$CH_3\cdot CMe{:}CH\cdot CMe{:}CHX$	no addition	[X = CO_2R]	

* Not exactly determined.

of the δ-methyl group, or introduction of a β-methyl group, represses αβ-addition, (*b*) introduction of β- *and* δ-methyl groups, or introduction of an α-carbonyl group, represses *both* αβ- and αδ-addition, and (*c*) introduction of a γ-methyl group, or replacement of the carboxylic activating group by acetyl, strongly augments αβ-addition. Modification of the ester addendum appears, as might be expected, only to affect the ease of addition.

J. Bloom and C. K. Ingold [21] regard Farmer and Mehta's results and certain supplementary results which they furnish relating to α-methylsorbic ester (not more than 2% αβ-addition), cinnamylidene-acetic ester (entirely or almost entirely αβ-addition), and styryl-cinnamic ester (little or no addition) as definitely supporting the view that the reagent attacks in the form of its anion. They assume that the conductivity of unsaturated ions, including dipolar ions, guarantees the distribution between C_δ and C_β of the positive charge produced by the primary polarisation, whilst the greater lability of double-bond electrons than of single-bond electrons determines the dominant reactivity of C_δ :

$$R\rightarrow \underset{\delta}{CH}=\underset{\gamma}{CH}\rightarrow \underset{\beta}{CH}=\underset{\alpha}{CH}\rightarrow CO_2R'$$

This holds provided the conditions of substitution in the $C_\delta : C_\gamma$- and $C_\beta : C_\alpha$-units, which determine the respective degrees of reversibility

[20] *J.*, 1930, 1610; 1931, 1904, 2561; *A.*, 1930, 1163; 1931, 1397.
[21] *Ibid.*, 1931, 2765; *A.*, 1391.

of the corresponding addition reactions, are comparable. The effect of modifying the existing state of substitution in the sorbic ester system should then be of the kind observed, the phenyl group exerting the orienting influence by virtue of its electron-releasing properties.

The formation, under suitable conditions of reaction, of an αβ-ester-addition product of ethyl muconate, almost entirely free from isomerides, has confirmed the view that the extensive production of αγ-products formerly noted is to be attributed to αβ, βγ-equilibration in the presence of sodium ethoxide.[22]

In hydrogen halide addition to conjugated compounds it might be anticipated that the hydrogen atom of the hydrogen halide molecule, probably as the ion, would initiate attack, and experiments intended to test this point have been carried out. Here, however, the possibility of attack at the β- (or β′-)carbon atom of the butadiene chain enters. Experiment shows that the mode of addition of hydrogen bromide to βγ- and αδ-dimethylbutadiene is compatible with reaction initiated at the terminal carbon atom, and completed in accordance with anionotropic principles.[23]

The same questions as to which ion or pole of the addendum molecule initiates reaction, and which atom of the conjugated molecules furnishes a seat of attack, enter into the consideration of additions by other unsymmetrical reagents such as iodine chloride. C. K. Ingold and H. G. Smith [24] find that this reagent, when added to butadiene, behaves in a way which might be anticipated on the basis of the mechanism imputed to bromine addition : [25] a mixture of $CH_2I{\cdot}CH{:}CH{\cdot}CH_2Cl$ and $CH_2I{\cdot}CHCl{\cdot}CH{:}CH_2$ is formed, conformably with the initial entrance of iodine at the α-carbon atom.

The results of I. E. Muskat and H. E. Northrup for the addition of chlorine to butadiene [26] confirm expectations based on known results for bromine addition,[27] as to the simultaneous formation of αβ- and αδ-dichlorides. Other statements of Muskat and his collaborators [28] relating to the γδ-hydrogenation of β-vinylacrylic

[22] E. H. Farmer and T. N. Mehta, *J.*, 1931, 1762; *A.*, 1037. Compare E. H. Farmer, *ibid.*, 1923, **123**, 3324.

[23] E. H. Farmer and F. C. B. Marshall, *ibid.*, 1931, 129; *A.*, 460. Further hydrobromination results (unpublished) obtained at the same time by these authors, which refer to piperylene and αα-dimethylbutadiene, can be best explained on the basis of hydrion attack initiated at the α- (or α′-) carbon atom.

[24] *Ibid.*, p. 2752; *A.*, 1391.

[25] *Ann. Reports*, 1928, **25**, 131.

[26] *J. Amer. Chem. Soc.*, 1930, **52**, 4043; A., 1930, 1553.

[27] E. H. Farmer, C. D. Lawrence, and J. F. Thorpe, *J.*, 1928, 729; *A.*, 1928, 504.

[28] I. E. Muskat and B. Knapp, *Ber.*, 1931, **64**, [*B*], 779; *A.*, 719; I. E. Muskat and L. Hudson, *J. Amer. Chem. Soc.*, 1931, **53**, 3178; *A.*, 1148.

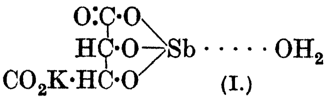
acid under catalytic conditions and the (apparently complete) formation of a $\gamma\delta$-addition product of the same acid with hypochlorous acid are inadequately established by the published experimental evidence : moreover, unpublished observations by the writer and his collaborators show that the statements only partially represent the facts.

Isomeric forms (two) of $\alpha\beta\gamma\delta$-tetrachlorobutadiene are obtained as a by-product in the preparation of trichloroethylene from tetrachloroethane by elimination of hydrogen chloride.[29] The formation of both saturated and unsaturated four-carbon molecules from hexachloroethane takes place apparently with moderate facility, but reversion to a two-carbon molecule (hexachloroethane) has only been accomplished by exhaustive chlorination of the halogenated diene.

Acids.

New instances of polymorphism amongst carboxylic acids and esters have been recognised. Malonic, succinic, and glutaric acids are dimorphous, the curve of transition points following a similar course to that of the melting points.[30] Ethyl palmitate, ethyl stearate, cetyl acetate, octadecyl acetate, ethyl cetylmalonate (as well as cetyl chloride) have also been found to be dimorphous.[31]

A new formula has been proposed for tartar emetic.[32] It is found that sodium antimonyl tartrate (tartar emetic itself is too insoluble for freezing-point determinations to be made) is present in the unimolecular condition in dilute aqueous solution, and it appears by analogy with α-phenylethylammonium and *p*-nitro-α-phenylethylammonium antimonyl tartrate, which contain no water of crystallisation, that the water of tartar emetic is not constitutive. Tartar emetic is only weakly acidic, but is easily esterified : consequently only one carboxyl group can be bound to antimony. The formula (I) is advanced which differs from Schiff's formula in the addition of a water molecule attached to antimony by a residual valency.


(I.)

It represents an unstrained condition as shown by models and is supported by the fact that the water molecule in barium antimonyl tartrate, although not in tartar emetic itself, is replaceable by pyridine, the product probably existing as the acid

[29] E. Müller and F. Hüther, *Ber.*, 1931, **64**, [*B*], 589; *A.*, 597.

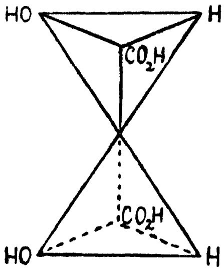
[30] F. D. la Tour, *Compt. rend.*, 1930, **191**, 1348; 1931, **193**, 180; *A.*, 1931, 198, 1036.

[31] J. W. C. Phillips and S. A. Mumford, *J.*, 1931, 1732; *A.*, 1003; J. C. Smith, *ibid.*, p. 802; *A.*, 684.

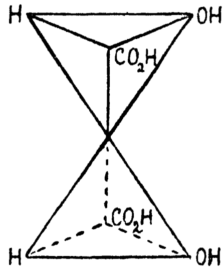
[32] H. Reihlen and E. Hezel, *Annalen*, 1931, **487**, 213; *A.*, 936.

[C_5H_5N $\cdots$ $SbC_4H_2O_6$]H in the solid state, and as the salt [H_2O $\cdots$ $SbC_4H_2O_6$]H,C_5H_5N in solution. The existence of the auxiliary valency in (I) is supported by the loss of water from the sodium salt in an evacuated vessel at room temperature (but from the potassium salt, only at 120°) and by the existence of the free acid only in the anhydrous form. Unlike the corresponding boron and arsenic compounds, tartar emetic is only slightly hydrolysed to $HK(C_4O_6H_4)$ and $Sb(OH)_3$, but its acid reaction is due to "intra-molecular hydrolysis."

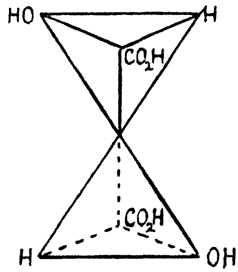
Measurements of the specific conductivity of the complexes formed by tartaric and boric acids in solution have led M. Amadori [33]



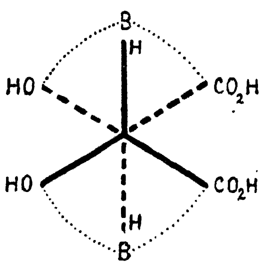
(I) Dextro.



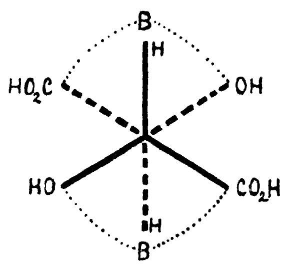
(II) Lævo.



(III) Meso.



(IV) Active.



(V) Inactive.

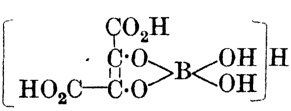
to the conclusion that the spatial disposition of the groups in the three tartaric acids is to be represented by the models (I, II, and III), rather than by the well-known Fischer models in which the carboxyl groups are on the same side of the molecule. It is considered that boric acid complexes are formed to about equal extents by the active and inactive acids and that they contain two ($\cdot O \cdot CH \cdot CO_2$)BOH groups which are disposed on opposite sides of the molecule; these groups if projected on to a plane normal to the axis of the central carbon atoms would have the relative dispositions indicated in figures IV and V.

[33] *Gazzetta*, 1931, **61**, 215; *A.*, 822.

Various views have been put forward with regard to the spontaneous decomposition of dihydroxymaleic acid in aqueous solution according to the equation

$$HO_2C{\cdot}C(OH){:}C(OH){\cdot}CO_2H \longrightarrow OH{\cdot}CH_2{\cdot}CHO + 2CO_2$$ [34]

The suggestions have in turn been made that the decomposition depends on hydration of the acid to trihydroxysuccinic acid, or the production of the bivalent negative ion $(C_4H_2O_6)''$, and consequently on the ionising power of the medium, on the production of the univalent negative ion $(C_4H_3O_6)'$, and finally on the concentration of the undissociated acid solvated on the carboxyl group. It is now shown from the relation existing between the velocity coefficient of decarboxylation and the degree of dissociation of the free acid, its lithium hydrogen salt, and lithium salt solutions of varying p_H, that the univalent ion $(C_4H_3O_6)'$ is the actively decomposing constituent.[35] The decomposition of the free acid appears to occur at $\frac{1}{40}$ the velocity for the ion and the ratio of the ionisation coefficients of the acid is that of a *trans*-acid of this series. Boric acid exerts a stabilising action proportional to its own concentration and that of the dihydroxy-acid, and a kinetic investigation points to the formation of an equimolecular complex. Organic solvents depress



the formation of the active ion and for the solvents water, acetonitrile, methyl alcohol, ethyl alcohol, and acetone the inverse proportionality of $- \log k$ (for decarboxylation) is established. The catalytic influence on the decomposition of the salts of heavy metals and of weak bases has also been studied.

Conditions for the catalytic hydrogenation of carboxylic acids and esters to the corresponding alcohols have been investigated by a number of workers.[36] Various catalysts (copper chromite, nickel, cobalt, copper, etc.) are used in conjunction with high pressures, and temperatures ranging from 250° to above 300°; at temperatures above 350° reduction can be carried to the hydrocarbon stage. It is not essential, however, for the smooth reduction of the carboxyl group to use high pressures, and provided a sufficiently active catalyst is employed[37] there is no hindrance to bringing about

[34] H. J. H. Fenton, *J.*, 1895, **67**, 774; 1905, **87**, 804; S. Skinner, *ibid.*, 1898, **73**, 483; A. Locke, *J. Amer. Chem. Soc.*, 1924, **46**, 1246; *A.*, 1924, i, 708.

[35] W. Franke and G. Brathuhn, *Annalen*, 1931, **487**, 1; *A.*, 936.

[36] W. Normann, *Z. angew. Chem.*, 1931, **44**, 714; *A.*, 1269; H. Adkins and K. Folkers, *J. Amer. Chem. Soc.*, 1931, **53**, 1095; *A.*, 598; W. Schrauth, O. Schenck, and K. Stickdorn, *Ber.*, 1931, **64**, [*B*], 1314; *A.*, 932.

[37] O. Schmidt, *Ber.*, 1931, **64**, [*B*], 2051; *A.*, 1268.

reduction at atmospheric pressure; thus, ethyl oleate in the presence of copper chromate at 270—280° yields octadecyl alcohol.

Oleic acid is convertible to the extent of 50% into elaidic acid by heating with sulphur;[38] erucic acid is likewise stated to be smoothly converted into brassidic acid when heated with 30% nitric acid and some sodium nitrite.[39] Oleic acid suffers oxidation by dilute permanganate solution into the corresponding elaido- and oleo-dihydroxystearic acids; both of these substances, as well as the corresponding dibromostearic acids, are resolvable through the strychnine salts; oleo-dichlorostearic acid is reported to yield with alcoholic potash stearolic acid and $\Delta^{\eta\iota}$-octadecadienoic acid, the latter of which is in turn convertible into stearolic acid by heating with the same reagent at a higher temperature.[40] From the parachor values obtained for oleic, elaidic, Δ^{β}-oleic, erucic and brassidic acids it is concluded that oleic and erucic acids have a *cis*-configuration whereas elaidic, Δ^{β}-oleic, and brassidic acids have a *trans*-configuration.[41] The hydroxyoleic acid from ergot oil has been investigated and found to be exactly similar in its physical constants and behaviour on oxidation to ricinoleic acid: the two substances are concluded to be identical.[42] *cis*- and *trans*-Forms of erucylacetic (Δ^{ξ}-tetracosenoic) acid have been synthesised, and the former found to be identical with nervonic acid.[43]

An observation which has an important bearing on current attempts to determine the constitution of the higher unsaturated fatty acids concerns the isomerisation of mono-olefinic esters during catalytic reduction. Methyl oleate, palmitoleate and erucate, when treated at 114—220° with insufficient hydrogen to produce complete saturation (nickel–kieselguhr catalyst), yield mixtures of esters in which unsaturated isomerides of the original esters occur; the double bond in these isomerides occupies a position adjacent to that it occupied in the original compounds, and both the original compounds and their isomerides appear to be present in *cis*- and *trans*-forms.[44] Possibly the isomerisation is to be attributed to the com-

[38] G. Rankov, *Ber.*, 1931, **64**, [*B*], 619; *A.*, 601.

[39] *Idem, J. pr. Chem.*, 1931, [ii], **131**, 293; *A.*, 1272.

[40] Y. Inoue and B. Suzuki, *Proc. Imp. Acad. Tokyo*, 1931, **7**, 261, 265; *A.*, 1271.

[41] G. B. Semeria and G. Ribotti-Lissone, *Gazzetta*, 1930, **60**, 862; *A.*, 1931, 149.

[42] H. Matthes and O. H. Kürschner, *Arch. Pharm.*, 1931, **269**, 88, 101; A., 602.

[43] J. B. Hale, W. H. Lycan, and R. Adams, *J. Amer. Chem. Soc.*, 1930, **52**, 4536; *A.*, 1931, 65.

[44] T. P. Hilditch and N. L. Vidyarthi, *Proc. Roy. Soc.*, 1929, [*A*], 122, 552; *A.*, 1929, 423; A. Steger and H. W. Scheffers, *Chem. Umschau*, 1931, **38**, 45, 61; *A.*, 711.

paratively high temperatures employed, since oleic acid is found to suffer isomerisation to the Δ^{ι}-acid when heated at 250° in contact with alumina;[45] at any rate the occurrence of isomerism presents a complicating factor in the determination by reductive procedures of the number and constitution of the polyolefinic acids which occur in natural products.

T. P. Hilditch and N. L. Vidyarthi have deduced from the nature of the oxidation products of partially hydrogenated methyl linoleate from soya bean and cotton seed oil that the unsaturation is of $\Delta^{\theta\lambda}$-type.[46] Y. Inoue and B. Suzuki have found by a similar method that a methyl *iso*linoleate derived from the oil of silkworm pupæ is also a $\Delta^{\theta\lambda}$-compound but differs from linoleic ester in having a *cis*-configuration about the $\theta\iota$-double bond.[47]

$$\begin{array}{rr} CH_3\cdot[CH_2]_4\cdot CH\!:\!CH\cdot CH_2\cdot CH & CH_3\cdot[CH_2]_4\cdot CH\!:\!CH\cdot CH_2\cdot CH \\ \| & \| \\ CH\cdot[CH_2]_7\cdot CO_2H & HO_2C\cdot[CH_2]_7\cdot CH \end{array}$$

Linoleic acid   iso*Linoleic acid*

By debrominating a solid tetrabromostearic acid prepared from poppy and soya bean oils, W. C. Smit[48] has obtained an oily linoleic acid (m. p. − 12° to − 11°) to which the $\Delta^{\theta\lambda}$-constitution is assigned; by thermal dehydration of ricinelaidic acid, however, he obtained a product consisting of a solid $\Delta^{\theta\kappa}$-compound (m. p. 54°) admixed with liquid (probably stereoisomeric) isomerides; likewise by the distillation of ricinoleic acid he obtained an oily mixture which appeared to contain both $\Delta^{\theta\lambda}$- and $\Delta^{\theta\kappa}$-linoleic acids, including a second form (m. p. 56°) of the $\Delta^{\theta\kappa}$-acid. The constitutions of the unsaturated acids were determined by ozonisation.

The conjugated $\Delta^{\theta\kappa}$-linoleic acid and its ethyl ester combine normally with maleic anhydride and by means of this reaction it has been verified that the dehydration product of ricinoleic acid contains both $\Delta^{\theta\lambda}$- and $\Delta^{\theta\kappa}$-linoleic acids (about 15% and 75% respectively).[49] Ethyl $\Delta^{\theta\kappa}$-linoleate when partially hydrogenated is stated to yield ethyl Δ^{ι}-elaidate, probably of the elaidic acid configuration.[50]

Earlier work on the partial hydrogenation of ethyl linolenate indicated that, although some isomerisation occurs in the process, the unsaturated centres are probably to be assigned to $\theta\iota$- and $\lambda\mu$-positions and also to a point beyond the fourteenth carbon atom of the chain.[46, 51] Later results obtained by partial hydrogenation

[45] K. H. Bauer and M. Krallis, *Chem. Umschau*, 1931, **38**, 201; *A.*, 1034.
[46] *Proc. Roy. Soc.*, 1929, [*A*], 122, 563; *A.*, 1929, 423.
[47] *Proc. Imp. Acad. Tokyo*, 1931, **7**, 15; *A.*, 601.
[48] *Rec. trav. chim.*, 1930, **49**, 539; *A.*, 1930, 891.
[49] J. Böeseken and R. Hoevers, *ibid.*, p. 1165; *A.*, 1931, 198.
[50] *Idem, ibid.*, p. 1161; A., 1931, 196.
[51] T. P. Hilditch, *Chem. Umschau*, 1930, **37**, 354; *A.*, 1931, 335.

methods indicated that the linolenic acid prepared from the solid hexabromide was a $\Delta^{\theta\lambda\xi}$-compound and suffered hydrogenation in stages, the $\theta\iota$- and ξo-linkings being reduced more readily than the $\lambda\mu$-linking; furthermore no migration of double linkings during hydrogenation was noticed.[52] It has since been concluded [53] that the Δ^{λ}-linking is first saturated, yielding $\Delta^{\theta\xi}$-octadecadienoic acid, from which the $\Delta^{\iota\nu}$-isomeride is formed by shifting of the unsaturated linkings. On treatment with 2 mols. of hydrogen the remote double linkings of these two diolefinic acids are saturated, forming Δ^{ι}- and Δ^{θ}-oleic acids, the latter of which yields the Δ^{η}- (and probably Δ^{ι}-) acid by isomerisation.

Couepic acid, a new isomeride of elæostearic acid, which occurs in the oil from *Couepia grandiflora*, gives oxidation products which indicate that the acid is a geometrical isomeride of the known α- and β-forms of elæostearic acid,

$$CH_3\cdot[CH_2]_3\cdot[CH{:}CH]_3\cdot[CH_2]_7\cdot CO_2H.$$ [54]

Behenolic acid has been synthesised from the undecenoic acid obtainable from castor oil.[55]

Ketones.

W. Bradley and R. Robinson [56] found that dibenzoylmethanes, $R\cdot CO\cdot CH_2\cdot CO\cdot R_1$, suffered fission by aqueous caustic soda in such a way that the stronger of the two acids $R\cdot CO_2H$ and $R_1\cdot CO_2H$ was in nearly all cases produced in the greater relative amount. The fission was considered to be a characteristic of the diketonic phases of the tautomeric system present and the hydrolysis was thought probably to result from the formation and decomposition of a complex anion as in the scheme :

$$R\cdot CO\cdot CH_2\cdot CO\cdot R_1 + \overset{\ominus}{O}H \longrightarrow R\cdot C(OH)(\overset{\ominus}{O})\cdot CH_2\cdot CO\cdot R_1 \longrightarrow$$
$$R\cdot C\overset{\ominus}{O}_2 + H\cdot CH_2\cdot CO\cdot R_1$$

Hence the chief factors controlling the change were taken to be (*a*) the rates of formation of the two possible complex ions and (*b*) the extent to which each of these breaks down with the formation of carboxylate ions.

Several recent researches bear directly on this question. Experiments on the alkaline hydrolysis ($0{\cdot}1N$-sodium hydroxide) and the

[52] K. H. Bauer and E. Ermann, *Chem. Umschau*, 1930, **37**, 241; *A.*, 1930, 1271.

[53] H. van der Veen, *ibid.*, 1931, **38**, 89; *A.*, 712.

[54] J. van Loon and A. Steger, *Rec. trav. chim.*, 1931, **50**, 936; *A.*, 1034; compare J. van Loon, *ibid.*, p. 638; *A.*, 822.

[55] R. Bhattacharya and J. L. Simonsen, *Proc. XV. Indian Sci. Cong.*, 1928, 153; *A.*, 1931, 1271.

[56] *J.*, 1926, 2356; *A.*, 1926, 1145.

acid alcoholysis (alcoholic hydrogen chloride) of nine unsymmetrical β-diketones of the general formula $CH_3\cdot CO\cdot CHR\cdot CO\cdot R'$ show that there is no relationship between the amounts of acid produced by fission and their strengths.[57] The hydrolysis and the alcoholysis figures differ considerably and it is suggested that the ratio of the amounts of $CH_3\cdot CO_2Et$ and $R\cdot CO_2Et$ produced by alcoholysis is a measure of the extent of enolisation of the respective carbonyl groups. Further experiments on the rate of alkaline alcoholysis (alcoholic sodium ethoxide) of six β-diketones and five β-ketonic esters [58] show that, although the ketonic esters are the more stable, the rate of alcoholysis of both diketones and ketonic esters increases very greatly with substitution on the carbon atom between the carbonyl groups. The rate of alcoholysis of the diketones has been measured in the presence both of hydrogen chloride and of sodium ethoxide and it is found that arrangement of the diketones in the order of decreasing reactivity with respect to acid alcoholysis presents them (with one exception) in the order of increasing reactivity towards alkaline alcoholysis. Diethyldibenzoylmethane, which cannot enolise, readily suffers alcoholysis and hydrolysis.

A. Michael and J. Ross [59] have formed the opinion that carbonyl derivatives which do not form enolates with alkali react primarily by addition of the alkali to the carbonyl group to form the group >C(OM)(OH). The slightly neutralised energy of the alkali in this complex loosens the affinity of the C-atom for the directly attached C-atoms so that cleavage can occur by hydrolysis. The rupture should take place at the carbon linking which is most weakened by the positive influence of the alkali atom. Fission, however, is not denied to enolic centres, and the fission of a sodium enolate by aqueous alkali is represented thus :

$$R\cdot CO\cdot CH\dot{:}C(ONa)R_1 + H_2O \longrightarrow R\cdot CO\cdot CH_2\cdot C(ONa)(OH)\cdot R_1 \longrightarrow R\cdot CO\cdot CH_3 + R_1\cdot CO_2Na$$

As regards the point of hydrolytic fission in the β-diketone molecule, it is considered that if the energy of the metal, in the alternatively formed enolates $R\cdot C(ONa)\dot{:}CH\cdot CO\cdot R_1$ and $R\cdot CO\cdot CH\dot{:}C(ONa)\cdot R_1$, is more effectively neutralised in the first than in the second, fission will occur preferentially at the enolic centre of the second; the point at which β-diketones are attacked by ordinary carbonyl reagents depends on whether the latter add more facilely to the carbonyl than

[57] W. M. Kutz and H. Adkins, *J. Amer. Chem. Soc.*, 1930, **52**, 4036; *A.*, 1930, 1559.

[58] *Idem, ibid.*, p. 4391; *A.*, 1931, 69. Compare N. L. Drake and R. W. Riemenschneider, *ibid.*, p. 5005; *A.*, 1931, 197.

[59] *Ibid.*, 1931, **53**, 2394; *A.*, 1035.

to the ·C(OH):C· group. Michael and Ross have also sought to show that "the principle of maximum neutralisation" satisfactorily explains the course of reaction in the alkylation of mixtures of enolic esters or of a substance such as α-acetyl-α'-carbethoxylsuccinic ester,[60] when the enolic centres in each instance are made to compete for sodium. The experimental results are striking and are held to show that the velocity relations applying to the action of alkyl halide upon the sodio-derivatives which are present, depend upon the *free* positive energy of the sodium : thus, the proportions of the sodium enolates present at the beginning of reaction become of importance only when the respective velocities of reaction are nearly equal.

All ketones which are structurally capable of enolisation, although not necessarily appreciably enolised under ordinary conditions, appear to suffer displacement of the keto-enol equilibrium in favour of the enolic forms in the presence of excess of Grignard reagents : the enolic forms are thereby fixed as magnesium organo-enolates and a volatile hydrocarbon is liberated.[61] Now when Grignard reagents interact with β-diketones, relatively normal products are obtained only from those compounds which are largely or entirely enolic.[62] Then *two* molecules of the reagent enter into reaction, liberating one molecule of hydrocarbon, thus :

$$\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}COPh} \xrightarrow{\mathrm{PhMgX}} \mathrm{Ph{\cdot}H + Ph{\cdot}C(OMgX){:}CH{\cdot}COPh} \xrightarrow{\mathrm{PhMgX}} \mathrm{Ph{\cdot}C(OMgX){:}CH{\cdot}CPh_2{\cdot}OMgX} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}CPh_2{\cdot}OH.}$$

If the diketones are added to only one equivalent of the reagent, half of the material is recovered unchanged. The little-enolised mono- and the di-substitution products of these simple diketones also react with two equivalents of the reagent. Addition takes place to one of the carbonyl groups and the resulting magnesium compound suffers fission :

$$\mathrm{Ph{\cdot}CO{\cdot}CHPh{\cdot}COPh} \xrightarrow{\mathrm{PhMgX}} \mathrm{Ph{\cdot}CO{\cdot}CHPh{\cdot}CPh_2(OMgX)} \longrightarrow \mathrm{Ph{\cdot}C(OMgX){:}CHPh + Ph_2CO} \xrightarrow{\mathrm{PhMgX}} \mathrm{Ph_3C(OMgX).}$$

A similar kind of cleavage takes place when oxido-ketones are treated with Grignard reagents.[63]

[60] The assumption that the position which the alkyl group ultimately occupies in this compound is necessarily that at which it enters during alkylation appears to be no more justified than the similar assumption with respect to the position taken up by the alkyl group of an alkylated addendum in the Michael reaction (compare p. 71).

[61] *Ann. Reports*, 1930, **27**, 100; V. Grignard and H. Blanchon, *Bull. Soc. chim.*, 1931, [iv], **49**, 23; *A.*, 465.

[62] E. P. Kohler and J. L. E. Erickson, *J. Amer. Chem. Soc.*, 1931, **53**, 2301; *A.*, 1060.

[63] E. P. Kohler, N. K. Richtmyer, and W. F. Hester, *ibid.*, p. 205; *A.*, 354.

The rôle of sodium in the acetoacetic ester condensation—whether as true condensing agent or as a mere generator of sodium ethoxide—has been the subject of renewed discussion. The fact is stressed that sodium produces two distinct types of reaction with aliphatic esters, *viz.*, the acetoacetic ester and the acyloin types of condensation.[64] The metal itself is considered to be the direct cause of the acyloin condensation and to produce at the same time sodium ethoxide :

$$2R{\cdot}CO_2Et \xrightarrow{2Na} ONa{\cdot}CR(OEt){\cdot}CR(OEt){\cdot}ONa \xrightarrow{2Na} ONa{\cdot}CR{:}CR{\cdot}ONa + 2NaOEt.$$

There are no data available to show whether the primary addition product reacts directly with more sodium or first loses sodium ethoxide to yield the free diketone; there is no need, however, to assume that reaction proceeds, when possible, through the enol form, or to postulate special mechanisms to account for the slowness of reaction of an ester which cannot enolise. With regard to the acetoacetic ester condensation it is deduced, from the proportions of acetoacetic ester, alcohol and hydrogen which are actually produced by the action of sodium on ethyl acetate, that the rôle of the metal is improbably other than that of a generator of sodium ethoxide, the latter being the real condensing agent.

It has been shown that the catalytic reduction of ethyl acetoacetate in the liquid phase in presence of a nickel catalyst yields mixtures of ethyl β-hydroxybutyrate and the condensation product $CHMe(OH){\cdot}CH_2{\cdot}CO_2{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2Et$.[65] The latter is the reduction product of the compound which is usually supposed to be an intermediate in the formation of dehydracetic acid and would point to the possibility that the formation of bimolecular reduction products of the kind in question is related to the enolising capacity of the particular acetoacetic ester employed, under the actual conditions of its reduction. This view is supported by the results of experiments in which no solvent, and solvents of different ionising power are employed, and by use of acetoacetic esters incapable of ionisation.

The function of the base employed as condensing agent in the Knoevenagel and allied reactions remains obscure in spite of several new investigations. The first stage of the union, without condensing agent, of formaldehyde with malonic ester (to yield hydroxymethylmalonic ester)[66] constitutes a bimolecular reaction, the velocity of

[64] J. M. Snell and S. M. McElvain, *J. Amer. Chem. Soc.*, 1931, **53**, 750, 2310; *A.*, 464, 1035. Compare B. B. Corson, W. L. Benson, and T. T. Goodwin, *ibid.*, 1930, **52**, 3988; *A.*, 1930, 1559.

[65] H. Adkins, R. Connor, and H. Cramer, *ibid.*, 1930, **52**, 5192; *A.*, 1931, 197.

[66] K. N. Welch, *J.*, 1931, 653; *A.*, 603; compare A. C. O. Hann and A. Lapworth, *ibid.*, 1904, **85**, 46; E. Hope and R. Robinson, *ibid.*, 1911, **99**, 2117.

which varies inversely as the hydrogen-ion concentration; if ammonia or trimethylamine is added as catalyst, the p_H value of the mixture not being allowed to change, little acceleration of the reaction ensues, but if piperidine is added rapid acceleration sets in. In the reaction between cinnamaldehyde and malonic acid (in aqueous alcohol), however, the velocity of reaction increases with increase in the hydrogen-ion concentration if the catalyst be one of various amino-acids; [67] moreover, urea and similar weak bases when dissolved in acetic acid are found to form very efficacious catalysts for the Knoevenagel reaction. The catalytic influence in the latter cases is imputed to the kation of the amino-acid or the kation of the highly-dissociated salt formed from the weak base and acetic acid.

In the Doebner reaction (more properly designated, it appears, the Verley reaction) the nature of the condensation product cannot be correlated with the order of the base employed.[68] Further, it is clear that the action of pyridine in yielding αβ-unsaturated acids is quite *abnormal* with respect to the general action of bases (even of other tertiary bases, or bases of similar strength) although, remarkably enough, the use of *traces* of pyridine leads to the production of normal βγ-unsaturated products. The catalytic activity of the base might presumably here also be imputed to the kation of a salt formed with malonic acid but could not generally be attributed to the lowering brought about by the base in the acidity of the medium.

W. Cocker, A. Lapworth, and A. T. Peters [69] show that the Pinner–Kötz theory with respect to the action of potassium cyanide and chloral in forming potassium dichloroacetate is capable of extension to cover a group of reactions including the conversion of cyanohydrins into amino-nitriles (a reaction proceeding by way of the free aldehyde or ketone), and the reversible formation of acetals. Some details with regard to the reactivity of ketones in acetal formation are recorded by G. F. Pfeiffer and H. Adkins.[70]

Oxidation Processes and Peroxides.

Several noteworthy attempts have been made to throw light on oxidation processes which employ or involve the formation of peroxide compounds: these comprise oxidations by ozone, by hydrogen peroxide, and auto-oxidation processes.

Ozonisation of an undiluted aldehyde gives rise to a mixture of the corresponding acid and peracid, containing the former in excess:

[67] K. C. Blanchard, D. L. Klein, and J. MacDonald, *J. Amer. Chem. Soc.*, 1931, **53**, 2809; *A.*, 1017.

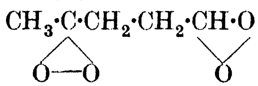
[68] S. E. Boxer and R. P. Linstead, *J.*, 1931, 740; *A.*, 935.

[69] *Ibid.*, p. 1382; *A.*, 1037.

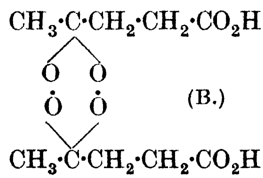
[70] *J. Amer. Chem. Soc.*, 1931, **53**, 1043; *A.*, 605.

in this way the whole of the ozone is used up ($2R{\cdot}CHO + O_3 \longrightarrow R{\cdot}CO_2H + R{\cdot}CO_3H$). On the other hand, ozonisation of the aldehyde in solution causes more extensive oxidation than is accounted for by the amount of ozone used; it is suggested in this case that ozone itself catalytically promotes interaction between the ozonide first formed and oxygen ($R{\cdot}CHO,O_3 + O_2 \longrightarrow R{\cdot}CO_2H + O_3$), and this behaviour probably also characterises the ozonisation of olefins in solution.[71]

From the form of ozone-absorption curves relating to unsaturated hydrocarbons treated with ozonised oxygen, G. Brus and G. Peyresblanques [72] have concluded that the primary products of reaction are normal ozonides and that the number of double linkings can be deduced from the data. Perozonide formation appears to occur subsequently, probably by addition of an atom of oxygen at the keto-group. A recent re-examination of the well-known " lævulic aldehyde diperoxide " of Harries [73] has shown that this substance is a decomposition product of caoutchouc ozonide, which is progressively formed when solutions of the latter are allowed to stand for a long time. It can be obtained in yields representing 15—20% of the carbon skeleton in the caoutchouc employed. In character it is acidic, peroxidic, but non-aldehydic: it does not behave as a peracid but yields lævulic acid (over 90% yield) on reduction with aluminium amalgam. The formula (A) of Harries is replaced by the bimolecular formula (B).



(A.)



(B.)

A. Rieche and his collaborators have shown that aldehydes readily unite with alkyl hydrogen peroxides to give monohydroxydialkyl peroxides, $R{\cdot}CH(OH){\cdot}O{\cdot}OR$, and with hydrogen peroxide itself to give hydroxyalkyl hydrogen peroxides, $R{\cdot}CH(OH){\cdot}O{\cdot}OH$, and the corresponding di-α-hydroxyalkyl peroxides. Ethylidene peroxide, it is interesting to note, could be obtained not only by dehydration of hydroxyethyl derivatives (mono- or di-), but also by warming butylene ozonide or by the auto-oxidation of ethyl ether. The mode of decomposition of these substances is described.[74]

[71] F. G. Fischer, H. Düll, and J. L. Volz, *Annalen*, 1931, **486**, 80; *A.*, 604.

[72] *Compt. rend.*, 1930, **190**, 501; *A.*, 1930, 449.

[73] R. Pummerer, G. Ebermayer, and K. Gerlach, *Ber.*, 1931, **64**, [*B*], 804; *A.*, 733.

[74] A. Rieche and F. Hitz, *ibid.*, 1930, **63**, [*B*], 2642; *A.*, 1930, 1554; A. Rieche and R. Meister, *ibid.*, 1931, **64**, [*B*], 2328, 2335; *A.*, 1267, 1268.

The oxidation of malonic, tartaric, maleic and similar dibasic acids by means of hydrogen peroxide at 100° proceeds through an acid–hydrogen peroxide complex but does not involve the formation of a peracid; [75] the oxidation of formaldehyde by acidified hydrogen peroxide is stated to yield either formic acid and hydrogen ($2CH_2O + H_2O_2 \longrightarrow 2H\cdot CO_2H + H_2$) or formic acid and water.[76]

Considerable interest attaches to the suggestion that the auto-oxidation of ethers proceeds by addition of molecular oxygen to the ethereal oxygen atom.[77] The immediate product is represented to be of oxonium type and suffers decomposition in two different ways :

$$(R\cdot CH_2)_2O \longrightarrow (R\cdot CH_2)_2\overset{\oplus}{O}\cdot O\cdot \overset{\ominus}{O} \longrightarrow R\cdot \overset{\oplus}{C}H_2 + R\cdot CH_2\cdot O\cdot O\cdot \overset{\ominus}{O}$$

$$\longrightarrow R\cdot CH_2\cdot O\cdot O\cdot O\cdot CH_2R \longrightarrow R\cdot CHO + H_2O$$

$$\xrightarrow{H_2O} R\cdot CH_2\cdot OH + R\cdot CH_2\cdot O\cdot O\cdot OH \longrightarrow R\cdot CH_2\cdot OH + R\cdot CHO + H_2O$$

Differences which have been observed in the behaviour of peracetic and perbenzoic acid towards unsaturated substances are now found to be only of secondary character: both reagents form primarily cyclic oxides, but fission of the oxide ring may occur subsequently under the conditions of reaction.[78] Solutions of peracetic acid have been applied to the determination of the degree of unsaturation in oils and fats [79] and it is claimed the method gives in the cases examined results which are in agreement with the Wijs iodine values and are more concordant than those obtained by the perbenzoic acid method of Nametkin and Abakumovski. Apparently, however, oxidation at the ethylenic linking does not inevitably occur with peracids,[80] since styryl methyl ketone is reported to yield β-phenylvinyl acetate with perbenzoic acid ($CHPh{:}CHAc \longrightarrow CHPh{:}CH\cdot OAc$). Oxidation of the acetylenic linking takes place less readily than is the case with the ethylenic linking and follows, when it occurs, a more complicated course of reaction.[81]

Polymerisation.

For many years opinion has been divided between the "*cyclo*-butane" formula of Kramer and Spilker for di*cyclo*pentadiene, and the *cyclo*hexene formula of Wieland. The isolation of *cyclo*pentane-

[75] W. H. Hatcher and W. H. Mueller, *Canadian J. Res.*, 1930, **3**, 291; *A.*, 1930, 1558.

[76] H. S. Fry and J. H. Payne, *J. Amer. Chem. Soc.*, 1931, **53**, 1973; *A.*, 819.

[77] N. A. Milas, *ibid.*, p. 221; *A.*, 334.

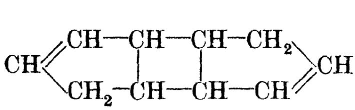
[78] J. Böeseken and G. C. C. C. Schneider, *J. pr. Chem.*, 1931, [ii], **131**, 285; *A.*, 1150.

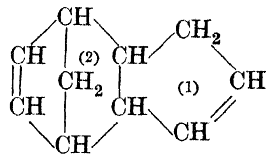
[79] W. C. Smit, *Rec. trav. chim.*, 1930, **49**, 691; *A.*, 1930, 1020.

[80] J. Böeseken and A. Kremer, *ibid.*, 1931, **50**, 827; *A.*, 1050.

[81] J. Böeseken and G. Slooff, *ibid.*, 1930, **49**, 95; *A.*, 1930, 322.

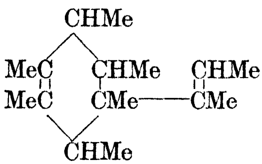
1 : 3-dicarboxylic acid from amongst the oxidation products of the dihydrogenated dimeride shows that Wieland's formula is correct.


(Kramer and Spilker)

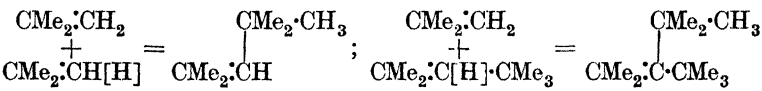

(Wieland)

Thus dimerisation of a simple cyclic butadiene is now definitely known to follow the course which is characteristic of the open-chain butadienes.[82] Further polymerisation, leading to the formation of tri-, etc., *cyclo*pentadienes, probably occurs at the reactive ethylene linking in ring (2).

The dimeride of isoprene, obtained together with dipentene and caoutchouc by heating the hydrocarbon alone or with acetic acid,[83] is a 1 : 3-menthadiene; formerly this compound was regarded by Harries as a dimethyloctatriene. Similarly the dimeride obtained by heating αβγδ-tetramethylbutadiene with concentrated formic acid is the methylpropenylhexamethyl*cyclo*hexene (I).[84]


(I.)

Degradation of the tri*iso*butylene prepared by the action of sulphuric acid on *tert.*-butyl alcohol indicates that the polymeride is produced in conformity with the additive mechanism indicated in the scheme:



Two additional isomerides of the final product appear, however, to be formed, and these could arise if double-bond movement occurred at the dimeride, and at both dimeride and trimeride stages of the polymerisation, respectively.[85]

If polymerisation of this type be considered to apply to butadienoid hydrocarbons, it is obvious that by taking into account both αβ- and αδ-types of addition, long polymeric chains could be formulated in which the same *iso*pentene unit occurs indefinitely but the end groups

[82] K. Alder, G. Stein, and H. Finzenhagen, *Annalen*, 1931, **485**, 223; *A.*, 473.

[83] T. Wagner-Jauregg, *ibid.*, 1931, **488**, 176; *A.*, 1031.

[84] P. van Romburgh and G. van Romburgh, *Proc. K. Akad. Wetensch. Amsterdam*, 1931, **34**, 224; *A.*, 819.

[85] R. J. McCubbin, *J. Amer. Chem. Soc.*, 1931, **53**, 356; *A.*, 333.

change according to the additive scheme adopted. Thus, if for the unsymmetrical compound, isoprene, it be assumed that the addendum molecule may (in effect) divide in the manner

$$H—CH{:}CH{\cdot}CMe{:}CH_2 \quad or \quad H—CH{:}CMe{\cdot}CH{:}CH_2$$

and add at the αβ- *or* αδ-positions of the conjugated monomeride, dimeride, etc., hydrocarbon, then six formulations become possible in which the unit ($CH_2{\cdot}CH{:}CMe{\cdot}CH_2$) = U recurs but the end groups change; in this way the polymerides (A), (B), (C), etc., are formed : [86]

(A) $CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}[U]_x{\cdot}CH{:}CMe{\cdot}CH{:}CH_2$
(B) $CH_2{:}CH{\cdot}CHMe{\cdot}CH_2{\cdot}[U]_x{\cdot}CH{:}CMe{\cdot}CH{:}CH_2$
(C) $CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}[U]_x{\cdot}CH{:}CMe{\cdot}CH{:}CH_2$

On ozonolysis such substances should yield not only large quantities of lævulaldehyde, lævulic acid, and lævulic acid peroxide, but small quantities of one or more of formaldehyde, pyruvaldehyde, acetaldehyde or the corresponding acids, etc.

The recognition of these end groups and their accurate quantitative estimation in relation to the quantity of lævulaldehyde and the derivatives thereof formed at the same time would give definite information concerning the non-cyclic nature of the polymeride, its molecular weight, and the mechanism of its formation. A new attempt to identify and estimate the ozonolysis products of caoutchouc [87] has demonstrated the formation of the lævulic series of products to an extent corresponding to nearly 90% of the carbon skeleton of the polymeride; in addition, small quantities of acetic acid, acetone (regarded as an impurity), a substance fermentable by yeast, carbon dioxide, formic acid, and succinic acid, have been recognised. Now, although none of the minor products can be definitely stated to have its origin in an end group, there is little doubt that at least 2% of the acetic acid produced is a primary fission product of caoutchouc, and not merely a decomposition product of lævulic acid; the origin of the fermentable substance (possibly pyruvic acid) is still in doubt. The statement of Harries *à propos* of the cyclic formula for rubber, that no ozone fission products containing less than five carbon atoms were to be obtained, is plainly ill-founded. The question of terminal groups remains open and its solution awaits further improvement of experimental technique.

The polymerisation of many substances is actively catalysed by ozonides and peroxides. Ozonised mixtures of two *iso*butylenes have been found to accelerate the polymerisation of styrene, indene, βγ-dimethylbutadiene, and furfuryl alcohol but not of stilbene,

[86] G. S. Whitby, *Trans. Inst. Rubber Ind.*, 1929, **5**, 190.
[87] R. Pummerer, G. Ebermayer, and K. Gerlach, *Ber.*, 1931, **64**, [*B*], 809; *A.*, 733.

o-hydroxybenzyl alcohol, and β-methyl-Δ^{β}-butene.[88] The velocity of polymerisation generally increases with increasing concentration of the catalyst up to 2%; moreover the catalytic activity is inherent in the original ozonides, and not in any decomposition products, since the activity diminishes rapidly on keeping. The polymerisation of unsaturated hydrocarbons is strongly accelerated by simultaneously occurring auto-oxidation processes—more effectively, indeed, than is accomplished by addition of peroxides.[89] Probably the actual catalysts in these cases are primary peroxides which have a more powerful accelerating action than that of the polymeric peroxides ultimately found among the polymerisation products. Polymerisation and peroxide-formation (polymeric) take place side by side, in proportions varying with the chemical constitution of the unsaturated compound and the availability of oxygen.

When acrylic acid is polymerised by irradiation, non-homogeneous, amorphous products result. Polymerisation is considered to follow the scheme:

$$\cdots\cdot CH(CO_2H)\cdot CH_2\cdot\cdots + xCO_2H\cdot CH{:}CH_2 \longrightarrow$$
$$\cdot CH(CO_2H)\cdot CH_2\cdot[CH(CO_2H)\cdot CH_2]_{x-1}\cdot CH(CO_2H)\cdot CH_2\cdot$$

Similarly, irradiation of vinyl acetate in chloroform is stated to yield a product of the type $Me\cdot CH(OR)\cdot[CH_2\cdot CH(OR)]_x\cdot CH_2\cdot CHCl_2$. The properties of these polymerides and of polyvinyl alcohols are described.[90] Further details are available with respect to the formation of polyoxymethylenes from formaldehyde[91] and it has been shown that polymerisation of aqueous formaldehyde with calcium hydroxide yields a solution which contains pentoses, hexoses, and possibly some heptoses.[92]

Nitrogen Compounds.

The synthesis of the simple amino-acids and their derivatives has attracted so large a measure of attention that it is impossible in the space at the writer's disposal to do more than indicate the main groups of compounds which have formed the subject of investigation.

Improved methods of carrying out the Strecker and Kolbe synthesis of α-amino-acids have been described in detail;[93] methods

[88] R. C. Houtz and H. Adkins, *J. Amer. Chem. Soc.*, 1931, **53**, 1058; *A.*, 597.

[89] H. Staudinger and L. Lautenschläger, *Annalen*, 1931, **488**, 1; *A.*, 1031.

[90] H. Staudinger and H. W. Kohlschütter, *Ber.*, 1931, **64**, [*B*], 2091; *A.*, 1270; H. Staudinger and A. Schwalbach, *Annalen*, 1931, **488**, 8; *A.*, 1032.

[91] H. Staudinger, R. Signer, and O. Schweitzer, *Ber.*, 1931, **64**, [*B*], 398; *A.*, 465.

[92] P. Karrer and E. von Krauss, *Helv. Chim. Acta*, 1931, **14**, 820; *A.*, 1037.

[93] W. Cocker and A. Lapworth, *J.*, 1931, 1391; *A.*, 943.

for preparing α-amino-acids and amides,[94] *N*-alkylated β-amino-esters,[95] γ-amino-,[96] ω-amino-,[97] and various dimethylamino- and bisdimethylamino-[98] derivatives of fatty acids have been worked out; and syntheses of *dl*-aspartic acid,[99] creatine and alacreatine,[1] serine,[2] ethyl aminomalonate and its derivatives,[3] derivatives of lysine,[4] and various aminohydroxy-[5] and hydroxyamino-acids [6] have been recorded. The formylation of amino-acids,[7] their acetylation by keten,[8] and the preparation of glycerol esters therefrom have also been studied.[9]

A series of investigations by A. Skita and F. Keil and their collaborators [10] deals with the production of the more complex amines by the catalytic reduction of carbonyl compounds in the presence of simple amines. In most cases colloidal platinum is used as catalyst. Schiff's bases, or mixtures of the aldehyde and primary amines from which the bases are formed, yield secondary amines on reduction; aldehydes of high molecular weight give secondary amines with ammonia, but the simpler aldehydes yield tertiary amines. Ketones react usually with aliphatic amines to produce *N*-substituted imines which are further reducible to secondary amines: under suitable conditions, however, substantial amounts

[94] T. Curtius and others, *J. pr. Chem.*, 1930, [ii], **125**, 211; *A.*, 1930, 752; H. Krause, *Chem.-Ztg.*, 1931, **55**, 666; *A.*, 1402; W. Cocker and A. Lapworth, *J.*, 1931, 1894; *A.*, 1402; R. Locquin and V. Cerchez, *Bull. Soc. chim.*, 1930, [iv], **47**, 1386; *A.*, 1931, 338; D. M. Birosel, *J. Amer. Chem. Soc.*, 1931, **53**, 3039; *A.*, 1149; P. S. Yang and M. M. Rising, *ibid.*, p. 3183; *A.*, 1150.

[95] J. Décombe, *Compt. rend.*, 1930, **191**, 945; *A.*, 1931, 76.

[96] A. Müller and E. Feld, *Monatsh.*, 1931, **58**, 22; *A.*, 943.

[97] B. Flaschenträger with F. Halle, T. Hosoda, F. Gebhardt, and B. Blechman, *Z. physiol. Chem.*, 1930, **192**, 245, 249, 253, 257; *A.*, 1931, 76.

[98] V. Prelog, *Coll. Czech. Chem. Comm.*, 1930, **2**, 712; *A.*, 1931, 204.

[99] M. S. Dunn and B. W. Smart, *J. Biol. Chem.*, 1930, **89**, 41; *A.*, 1931, 76.

[1] H. King, *J.*, 1930, 2374; *A.*, 1930, 563.

[2] S. K. Mitra, *J. Indian Chem. Soc.*, 1930, **7**, 799; *A.*, 1931, 205.

[3] R. Locquin and V. Cerchez, *Bull. Soc. chim.*, 1930, [iv], **47**, 1274, 1282, 1287, 1377, 1381; 1931, [iv], **49**, 42, 47; *A.*, 1931, 205, 338, 471.

[4] R. Enger and H. Steib, *Z. physiol. Chem.*, 1930, **191**, 97; *A.*, 1930, 1419; R. Enger and F. Halle, *ibid.*, p. 103; *A.*, 1930, 1420; R. Enger, *ibid.*, p. 117; *A.*, 1930, 1420.

[5] W. J. N. Burch, *J.*, 1930, 310; *A.*, 1930, 460.

[6] L. W. Jones and R. T. Major, *J. Amer. Chem Soc.*, 1930, **52**, 1078; *A.*, 1930, 754; M. Tomita and J. Karashima, *Z. physiol. Chem.*, 1930, **187**, 238; *A.*, 1930, 585.

[7] R. E. Steiger, *J. Biol. Chem.*, 1930, **86**, 695; *A.*, 1930, 752.

[8] M. Bergmann and F. Stern, *Ber.*, 1930, **63**, [*B*], 437; *A.*, 1930, 459.

[9] L. Haskelberg, *Compt. rend.*, 1930, **190**, 270; *A.*, 1930, 328.

[10] *Ber.*, 1928, **61**, [*B*], 1452, 1682; 1929, **62**, [*B*], 1142; *A.*, 1928, 1120, 1228; 1929, 808; *Monatsh.*, 1929, **53**, 753; *A.*, 1929, 1436; *Ber.*, 1930, **63**, [*B*], 34; *A.*, 1930, 327.

of primary amines may arise. From diketones and primary amines, *N*-substituted amino-alcohols can be obtained; in this way α-phenylpropane-αβ-dione, when reduced together with methylamine, gives ephedrine—a method of preparation for the latter which had been independently employed by R. H. F. Manske and T. B. Johnson.[11] Tertiary amines are formed by the reduction of nitriles, alone or in the presence of ketones, and in some cases also by the reduction of aldehydes admixed with secondary amines.

Acylvinyl- and arylvinyl-amines of the general formula

$$R\cdot CO\cdot CH{:}CH\cdot NR_1R_2$$

may be conveniently prepared by the action of ammonium chloride or the hydrochloride of an amine on the sodium salt of aliphatic and aromatic hydroxymethylene ketones.[12]

By the action of dry hydrogen sulphide on dry amines (usually in ether at 0°) M. Achterhof, R. F. Conaway, and C. E. Boord have prepared a series of amine hydrogen sulphides.[13] The salts from the more volatile amines decompose in air, giving sulphur, but those from the less volatile amines suffer oxidation to the corresponding thiosulphates.

The structure of sphingosine derived from cerebroside mixtures has been the subject of renewed investigation.[14] It is now found that, whereas the ozonolysis of triacetylsphingosine yields tetradecoic acid (and aldehyde) together with α-amino-βγ-dihydroxy-*n*-butyric acid, the oxidation of dihydrosphingosine yields palmitic acid; moreover the oxidation of sphingosine sulphate also gives tetradecoic acid. It is concluded, therefore, that sphingosine has the constitution $CH_3\cdot[CH_2]_{12}\cdot CH{:}CH\cdot CH(NH_2)\cdot CH(OH)\cdot CH_2\cdot OH$.

New derivatives of asparaginedialdehyde [15] and hydrazinopropaldehyde [16] have been obtained and many new examples of the formation of hydrazides, azides, and carbamides of mono- and poly-carboxylic acids and lactones are furnished by the researches of T. Curtius and his collaborators.[17]

Muscarine has been successfully purified by the precipitation and

[11] *J. Amer. Chem. Soc.*, 1929, **51**, 580; *A.*, 1929, 441.

[12] E. Benary, *Ber.*, 1930, **63**, [*B*], 1573; *A.*, 1930, 1026.

[13] *J. Amer. Chem. Soc.*, 1931, **53**, 2682; *A.*, 1041.

[14] E. Klenk, *Z. physiol. Chem.*, 1929, **185**, 169; *A.*, 1930, 73; E. Klenk and W. Diebold, *ibid.*, 1931, **198**, 25; *A.*, 829.

[15] A. Wohl and E. Bernreuther, *Annalen*, 1930, **481**, 1; *A.*, 1930, 1021.

[16] A. Wohl and A. Pranschke, *Ber.*, 1931, **64**, [*B*], 1381; *A.*, 937.

[17] T. Curtius, G. von Brüning, and H. Derlon, *J. pr. Chem.*, 1930, [ii], **125**, 63; *A.*, 1930, 766; T. Curtius and W. Sandhaas, *ibid.*, p. 90; *A.*, 1930, 757; T. Curtius and H. Sauerberg, *ibid.*, p. 139; *A.*, 1930, 757; T. Curtius, W. Sieber, F. Nadenheim, O. Hambsch, and W. Ritter, *ibid.*, p. 152; *A.*, 1930, 755; T. Curtius and W. Dörr, *ibid.*, p. 425; *A.*, 1930, 756.

crystallisation of its salt with the radical $[(NH_3)_2Cr(SCN)_4]^-$; analysis of the salt indicates the formula $[C_8H_{18}O_2N]^+$ for the muscarine ion. Since muscarine contains a hydroxy-group, gives trimethylamine and dihydroxy-*n*-valeric acid by the Hofmann degradation, and behaves as an aldehyde, it is considered to have the constitution $OH{\cdot}CHEt{\cdot}CH(CHO){\cdot}NMe_3{\cdot}OH$ or (less probably)

$$CHO{\cdot}CH(OH){\cdot}CHEt{\cdot}NMe_3{\cdot}OH.$$[18]

Cystine may be satisfactorily reduced to cysteine by the action of sodium in liquid ammonia,[19] by aluminium amalgam in aqueous solution,[20] or catalytically in the presence of spongy palladium.[21] Treatment of a solution of cystine in dilute sulphuric acid with silver sulphate, followed by neutralisation to p_H 5—6, causes precipitation of 70—85% of the total nitrogen in the form of a compound $(C_3H_5O_2NSAg)_2,Ag_2SO_4$. Decomposition of this compound with hydrochloric acid yields a solution containing more than 90% of its nitrogen in the form of cysteine.[22] The silver compound differs from the apparently normal silver salt of cystine and is regarded as a silver mercaptide.

The question of the ketimine-enamine tautomerism of β-amino-acrylic esters has been examined by K. von Auwers and W. Susemihl[23] with the aid of refractivity determinations. Ketimino-forms, because they contain no conjugated system, should display normal optical behaviour: enamines, on the other hand, with the system $N{\cdot}C{:}C{\cdot}C{:}O$, should exhibit marked exaltation. The optical data, particularly in the case of ethyl β-aminocrotonate and its derivatives, are shown to be in harmony with the constitution

$$NHR{\cdot}CMe{:}CH{\cdot}CO_2Et,$$

but cannot be explained in relation to the alternative structures $NR{:}CMe{\cdot}CH_2{\cdot}CO_2Et$ and $\begin{matrix}CHMe\\ |\\ NH\end{matrix}\!\!>\!CH{\cdot}CO_2Et$. Marked differences are observed between the keto-enolic and ketimine-enamine types of tautomerism, since in the latter type an equilibrium mixture dependent on the nature of the compound and the external conditions does not appear to exist in the molten material in which the enamine form predominates. The conditions which determine the degree of enolisation in oxygen compounds appear to be little, if at all, active with corresponding nitrogen compounds.

[18] F. Kögl, H. Duisberg, and H. Erxleben, *Annalen*, 1931, **489**, 156; *A.*, 1279.

[19] V. du Vigneaud, L. F. Audrieth, and H. S. Loring, *J. Amer. Chem. Soc.*, 1930, **52**, 4500; *A.*, 1931, 76.

[20] E. Gebauer-Fülnegg, *ibid.*, p. 4610; *A.*, 1931, 76.

[21] M. Bergmann and G. Michalis, *Ber.*, 1930, **63**, [*B*], 987; *A.*, 1930, 754.

[22] H. B. Vickery and C. S. Leavenworth, *J. Biol. Chem.*, 1930, **86**, 129; *A.*, 1930, 754.

[23] *Ber.*, 1930, **63**, [*B*], 1072; *A.*, 1930, 897.

According to A. Hantzsch, a comparison of the ultra-violet absorption of trichloroacetamide, its piperidine-derivative, $CCl_3\cdot CO\cdot NC_5H_{10}$, and the iminoether $CCl_3\cdot C(OMe)\colon NH$ in methyl alcohol, water, and chloroform indicates that the equilibrium $CCl_3\cdot CO\cdot NH_2 \rightleftharpoons CCl_3\cdot C(OH)\colon NH$ is displaced extensively to the right in chloroform and further in water; similarly, benzamide appears to be almost completely dissolved as the iminohydrin Ph·C(OH):NH.[24] Comparison of the boiling points of the amides, methylamides, and iminoethers shows that amides and methylamides exist mainly in the iminohydrin form R·C(OH):NH and R·C(OH):NMe. The anomalies in the boiling points of the amides and methylamides are attributed to association caused by the presence of the hydroxyl groups and consequent difficulty in passing into the unimolecular condition. In contrast to the acid amides, thioacetamide appears to be present as the true thioamide $CH_3\cdot CS\cdot NH_2$ in chloroform or ether and only to a minor extent as the iminothioether in water.

Hantzsch further considers that the two additive products derivable from hydrogen halides and nitriles are respectively identical with the products obtained by the interaction of amides and phosphorus pentachloride and hitherto regarded as imide chlorides, R·CCl:NH, and amide chlorides, $R\cdot CCl_2\cdot NH_2$.[25] They are actually nitrilium salts, the former being monohalides [R·C≡NH]Cl, and the latter dihalides [R·C≡NH]Cl,HCl, in which the second acid molecule is not structurally combined. Nitriles dissolved in concentrated sulphuric acid are present as completely dissociated sulphates $[R\cdot C\equiv NH]SO_4H$; amides also when dissolved by sulphuric acid yield completely dissociated sulphates. Aromatic amides are considered to yield iminohydrinium salts $[Ar\cdot C(OH)\colon NH_2]SO_4H$ in conformity with the view that the free amides are preponderatingly iminohydrins, R·C(OH):NH; the true tertiary amides, $Ar\cdot CO\cdot NR_2$, however, also yield similarly constituted iminohydrinium salts. The transformation of nitrilium sulphate into iminohydrinium sulphate takes place slowly but completely at the ordinary temperature. The conversion of nitrile into amide in aqueous solution depends on the formation of nitrilium salts, which pass by addition of water into iminohydrinium salts: these are hydrolysed to amides.

A ketenimino-structure is also supposed to be assumed by acetonitrile in reacting with ethylmagnesium bromide, the product,

[24] *Ber.*, 1931, **64**, [*B*], 661; *A.*, 608.
[25] *Ibid.*, p. 667; *A.*, 608; compare J. Verhulst, *Bull. Soc. chim. Belg.*, 1930, **39**, 563; *A.*, 1931, 471.

$CH_2{:}C{:}N{\cdot}MgBr$, reacting with water (addition at the ethylenic linkage) to yield some acetamide.[26]

Saturated nitriles are obtainable in good yield by passing many of the members of the fatty acid series, together with ammonia, over heated silica gel.[27] New details relating to the preparation of a number of αβ-(*cis*- and *trans*-) and βγ-unsaturated nitriles [28] are recorded.

It is a matter of considerable interest that hydrogen chloride has been found to combine with liquid (or dissolved) hydrogen cyanide, to yield the sesquichloride 2HCN,3HCl; hydrogen bromide and iodide also yield sesquihalides with hydrogen cyanide, but the formation of no such compound as HCN,HCl has been observed.[29] The sesquichloride, when heated alone or with liquid hydrogen cyanide, or when kept in a vacuum over sodium hydroxide, was found to yield chloromethyleneformamidine, $NH{:}CH{\cdot}N{:}CHCl$, a hygroscopic solid: this when heated with quinoline yielded a bimolecular hydrogen cyanide—evidently imidoformylcarbylamine, $NH{:}CH{\cdot}N{:}C$.

Mono-, Di- and Tri-saccharides.

In last year's Report reference was made to C. S. Hudson's contention that change of ring form may and does occur during the methylation of sugars, certain of W. N. Haworth's conclusions respecting the structural representation of the sugars thereby being vitiated. The validity of the principle of optical superposition, as utilised by Hudson in arriving at his suggested formulæ for certain of the mono- and di-saccharides, has been examined by W. N. Haworth and E. L. Hirst in considerable detail and it is shown that reliance on the principle in classifying the sugars leads to serious inconsistencies and necessitates the postulation of structures at variance with the bulk of the experimental evidence.[30]

In particular, Hudson ascribes to α-mannose and α-methylmannoside a different ring structure from that of β-mannose and α- and β-glucose and their glucosides and tetra-acetates, and assumes

[26] G. Mignonac and C. Hoffmann, *Compt. rend.*, 1930, **191**, 718; *A.*, 1930, 1564.

[27] J. A. Mitchell and E. E. Reid, *J. Amer. Chem. Soc.*, 1931, **53**, 321; *A.*, 339.

[28] R. Breckpot, *Bull. Soc. chim. Belg.*, 1930, **39**, 462; *A.*, 1931, 194; G. Heim, *ibid.*, p. 458; *A.*, 1931, 205; P. Colmant, *ibid.*, p. 568; *A.*, 1931, 472; P. Bruylants and H. Minetti, *Bull. Acad. roy. Belg.*, 1930, [v], **16**, 1116; *A.*, 1931, 205; P. Bruylants, *ibid.*, 1931, [v], **17**, 1008; *A.*, 1403; P. Bruylants and L. Ernould, *ibid.*, p. 1027; *A.*, 1403.

[29] L. E. Hinkel and R. T. Dunn, *J.*, 1930, 1834; *A.*, 1930, 1421.

[30] *J.*, 1930, 2615; *A.*, 1931, 200; compare K. Freudenberg, *Sitzungsber. Heidelberger Akad. Wiss.*, 1931, No. 2, 3; *A.*, 825.

that the true structural isomeride of β-mannose (and α- and β-glucose, etc.) should be an unknown form of α-mannose having $[\alpha]_D + 77°$, since such a value would bring the rotational difference between this α- and the known β-form into line with those that are found for the two glucoses. Hudson's scheme moreover requires that this variety of α-mannose, and not the normal variety (+ 30°), occurs as a combined residue in 4-glucosido-α-mannose and in 4-galactosido-α-mannose.

It has now been conclusively proved by hydrolysis with emulsin that the mannoside residue in 4-glucosido- and 4-galactosido-α-methylmannoside is the normal pyranoside variety of α-methylmannoside and not the hypothetical form of Hudson; [31] moreover it has been demonstrated that both forms (α- and β-) of methylmannoside which are obtainable in the normal manner from mannose have an identical six-atom structure [32] and that derivatives of 4-glucosido- and 4-galactosido-mannose retain unimpaired their structural rigidity during methylation.[33] From the manner in which the optical rotatory power of different methylated lactones varies from solvent to solvent there can be little doubt that configurational relationships, *e.g.*, the *cis*- relationship of methoxyl groups in the methylated molecules, have a profound influence on the optical rotatory powers of substances which cannot alter their ring structure under the influence of solvent [34] and are to be looked to as the source of some of the observed discrepancies in correlating rotational data.

Other demonstrations of the presence of a pyranose structure refer to penta-acetyl β-*d*-mannose,[35] β-methylgalactoside,[36] glycuronic acid,[37] di*iso*propylidenegalactose,[38] and 5-methoxyketose.[39]

The phenomenon of acyl migration in sugars and polyhydric

[31] W. N. Haworth, E. L. Hirst, H. R. L. Streight, H. A. Thomas, and J. I. Webb, *J.*, 1930, 2636; *A.*, 1931, 200; W. N. Haworth, E. L. Hirst, (Miss) M. M. T. Plant, and R. J. W. Reynolds, *ibid.*, p. 2644; *A.*, 1931, 200. Compare H. S. Isbell, *Bur. Stand. J. Res.*, 1930, **5**, 1179; *A.*, 1931, 201.

[32] W. N. Haworth, E. L. Hirst, H. G. Bott, and R. S. Tipson, *J.*, 1930, 2653; *A.*, 1931, 200.

[33] W. N. Haworth, E. L. Hirst, and H. R. L. Streight, *ibid.*, 1931, 1349; *A.*, 939; W. N. Haworth, E. L. Hirst, and (Miss) M. M. T. Plant, *ibid.*, 1931, 1354; *A.*, 939.

[34] W. N. Haworth, E. L. Hirst, and J. A. B. Smith, *ibid.*, 1930, 2659; *A.*, 1931, 200.

[35] P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, 1931, **90**, 89; *A.*, 337.

[36] A. Müller, *Ber.*, 1931, **64**, [*B*], 1820; *A.*, 1039.

[37] J. Pryde and R. T. Williams, *Nature*, 1931, **128**, 187; *A.*, 1036.

[38] P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, 1931, **92**, 257; *A.*, 1276.

[39] E. F. Hersant and W. H. Linnell, *Quart. J. Pharm.*, 1931, **4**, 52; *A.*, 825.

alcohols has attracted further attention. Certain changes in the polarity of the acyl group appear to increase the tendency towards the formation of cyclic dioxolane derivatives by attracting the mobile hydrogen to the CO-group. β-Hydroxyethyl trichloroacetate, for instance, is unobtainable in the open-chain form : all attempts to prepare it yield the ortho-ester isomeride

$$\begin{matrix} CH_2{\cdot}O \\ | \\ CH_2{\cdot}O \end{matrix} > C < \begin{matrix} OH \\ CCl_3 \end{matrix} .$$

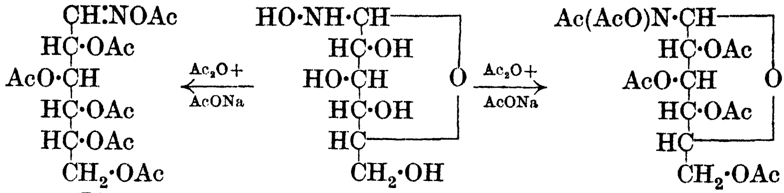
In other instances the strong tendency towards hydrogen migration facilitates fission of the acetate molecule into two molecules of aldehyde on heating, *e.g.*, benzyl trichloroacetate yields benzaldehyde and chloral ($CH_2Ph{\cdot}O{\cdot}CO{\cdot}CCl_3 \longrightarrow Ph{\cdot}CHO + CCl_3{\cdot}CHO$).[40]

New examples of the appearance of " γ "- or ortho-ester-forms of sugar acetates have been reported for triacetyl methyl-*d*-riboside [41] and hepta-acetyl 4-glucosidomethylmannoside [42] and migration of acetyl occurs during the methylation of 2 : 3 : 4-triacetyl α-methylglucoside.[43] The kinetics of acyl migration have been studied for solutions of 3-acetyl*iso*propylideneglucose by K. Josephson,[44] who finds that a proportionality exists between the rate of acyl migration and the concentration of hydroxyl ion over a considerable range of acidity. The " γ "-form of monoacetyl methylrhamnoside, however, is unstable in acid solution and the change whereby the glycosidic methyl group of this compound is hydrolysed, and the acetyl group transferred wholly to C_2, appears to be catalysed by hydrogen ions.[45]

Several interesting observations have been made with regard to the properties of the free aldehyde forms of sugars and the occurrence of the aldehyde phase in certain ordinary sugar reactions. Apparently the free aldehyde form of galactose is produced in the formation of the phenylhydrazone, since after acetylation the product is identical with the phenylhydrazone generated from penta-acetyl aldehydogalactose.[46] Also the ring form of glucose oxime would seem to open to the aldehydo-form when submitted to the Wohl procedure for the production of gluconpremitrile : at least, hexa-acetyl aldehydo-glucose oxime (I) is formed in the process and yields penta-acetyl gluconpremitrile by loss of acetic acid, whereas the cyclic

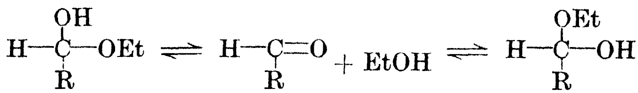
40 H. Hibbert and M. E. Greig, *Canadian J. Res.*, 1931, **4**, 254; *A.*, 820.
41 P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, 1931, **92**, 109; *A.*, 938.
42 H. S. Isbell, *J. Amer. Chem. Soc.*, 1930, **52**, 5298; *A.*, 1931, 201.
43 W. N. Haworth, E. L. Hirst, and (Miss) E. G. Teece, *J.*, 1931, 2858.
44 *Ber.*, 1930, **63**, [*B*], 3089; *A.*, 1931, 199.
45 W. N. Haworth, E. L. Hirst, and H. Samuels, *J.*, 1931, 2861.
46 M. L. Wolfrom and C. C. Christman, *J. Amer. Chem. Soc.*, 1931, **53**, 3413; *A.*, 1276.

hexa-acetyl β-glucose oxime (II) which is produced at the same time does not yield the nitrile when heated.[47]



(I.) (II.)

Penta-acetyl aldehydogalactose forms well-defined crystalline compounds with alcohol and with water. These, unlike the free penta-acetyl aldehydo-sugars themselves, show mutarotation in alcohol-free chloroform.[48] The curve for the alcoholate falls rapidly to a minimum and then increases rather less rapidly to a value higher than the original; its form points to the presence in solution of two semi-acetal individuals in equilibrium with the aldehyde and alcohol:



The aldehydrol, on the other hand, under like conditions shows only a steady fall in rotation along an exponential curve indicating a simple unimolecular decomposition into free aldehyde and water. Lactose phenylosazone also exhibits mutarotation in methyl alcohol but not in anhydrous alcohol-free solvents; the mutarotation of osazones does not appear to arise from tautomerism between dihydrazone and azo-forms, since fructose methylosazone, which does not possess a labile hydrogen atom, exhibits mutarotation.[48a]

Constitutions have been established, as the result of synthesis, of two natural glucosides: æsculin is formulated as 6-glucosidoxy-7-hydroxycoumarin [49] and euxanthic acid as the compound (I) in which the sugar residue is glycuronic acid, probably attached to the nucleus by a β-glucosidic linking.[50] In addition, the formulation of monotropitoside (gaultherin) as a primeveroside of methyl salicylate (III) has been synthetically demonstrated.[51]

The aldobionic acid from gum arabic, referred to in last year's Report, is now shown to be a glycuronosido-galactose in which the

[47] M. L. Wolfrom and A. Thompson, *J. Amer. Chem. Soc.*, 1931, **53**, 622; *A.*, 467.

[48] M. L. Wolfrom, *ibid.*, p. 2275; *A.*, 1039.

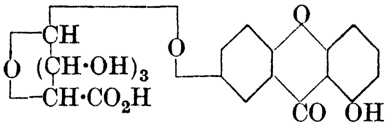
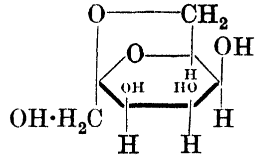
[48a] E. Votoček and F. Valentin, *Arhiv Hemiju*, 1931, **5**, 155; *A.*, 1274.

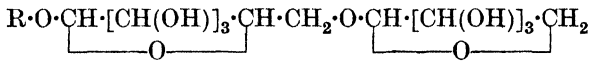
[49] F. S. Head and A. Robertson, *J.*, 1930, 2434; *A.*, 1931, 73.

[50] A. Robertson and R. B. Waters, *ibid.*, 1931, 1709; *A.*, 1040.

[51] *Idem*, *ibid.*, p. 1881; *A.*, 1400.

reducing group of the glycuronic acid residue is joined to the 6-position of the galactose residue.[52] Sedosan (anhydrosedoheptose) is formulated as the 2 : 7-anhydropyranose (II).[53]

(I.)   (II.)

 (III.)

(R = *o*-C_6H_4·CO_2Me.)

The hexosemonophosphate obtained by R. Robison through fermentation of glucose or fructose in presence of sodium phosphate is reported to be glucose-6-phosphate, which has now been synthesised from *iso*propylideneglucose; [54] methylation of Robison's product is reported to yield two distinct forms of the corresponding methylglycoside.[55]

The saccharals of epimeric sugars prove to be identical, as would be expected : *d*-glucal is identical with *d*-mannal, and *d*-xylal with *d*-lyxal.[56] It has also been found that tetra-acetyl hydroxyglucal yields the same osazone as tetra-acetyl hydroxygalactal,[57] and, by addition of chlorine, followed by hydrolysis, yields both tetra-acetyl glucosone hydrate and triacetyl glucosone hydrate.[58] Both glucal [59] and *ψ*-glucal [60] have pyranose structures, and the latter, which has the double bond in the 2 : 3-position, constitutes the unsaturated unit in *ψ*-cellobial; the reduction products of *ψ*-glucal and *ψ*-cellobial, *viz.*, 2 : 3-dideoxyglucose and 2 : 3-dideoxycellobiose, are also pyranose forms. It is suggested as the result of oxidation (hydroxylation) experiments with galactal that the group attached to the C_3-atom in glucals (*e.g.*, OH, OMe, or OAc) may have a directing influence on the spatial disposition of the hydroxyl group which

[52] S. W. Challinor, W. N. Haworth, and E. L. Hirst, *J.*, 1931, 258; *A.*, 465; see *Ann. Reports*, 1930, **27**, 109.

[53] H. Hibbert and C. G. Anderson, *Canadian J. Res.*, 1930, **3**, 306; *A.*, 1930, 1560.

[54] P. A. Levene and A. L. Raymond, *J. Biol. Chem.*, 1930, **89**, 479; 1931, **91**, 751; 1931, **92**, 757, 765; *A.*, 1931, 63, 933, 1148.

[55] E. J. King, R. R. McLaughlin, and W. T. J. Morgan, *Biochem. J.*, 1931, **25**, 310; *A.*, 600.

[56] M. Gehrke and F. Obst, *Ber.*, 1931, **64**, [*B*], 1724; *A.*, 1038.

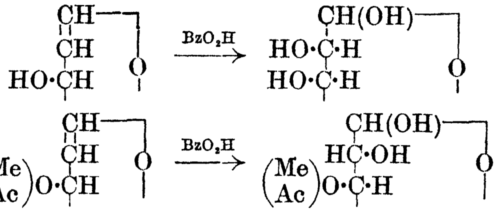
[57] M. Bergmann and L. Zervas, *ibid.*, pp. 1434, 2032; *A.*, 939, 1275.

[58] K. Maurer and W. Petsch, *ibid.*, p. 2011; *A.*, 1275.

[59] E. L. Hirst and C. S. Woolvin, *J.*, 1931 1131; *A.*, 1399.

[60] M. Bergmann and W. Freudenberg, *Ber.* 1931, **64**, [*B*], 158; *A.*, 336.

enters at the C_2-atom, thus being responsible for the predominating *cis-* or *trans*-dispositions at the C_2- and C_3-atoms produced in accordance with the scheme : [61]



Alcohols react with acetohalogeno-sugars (mono- or di-saccharides) in the presence of mercuric acetate to produce glycosides of the sugar acetates, the α- or β-configuration of which is to some extent governed by the proportions of the reactants.[62] By replacing the alcohol with a sugar derivative possessing one free hydroxyl group, the formation of the acetyl derivatives of di- and tri-saccharides can be effected with some control over the nature (α- or β-) of the glycosidic linking.[63] A somewhat similar method of coupling, employing silver carbonate, calcium chloride and iodine in place of mercury salts, has been applied to the synthesis of tri- and tetra-saccharide acetates.[64]

Recent observations in relation to turanose and melezitose [65] indicate that these sugars are more correctly represented by the structures originally assigned to them by G. Zemplén and G. Braun [66] than by those subsequently assigned by G. C. Leitch.[67] A new disaccharide, *neo*trehalose, synthesised from triacetyl glucose 1 : 2-anhydride and tetra-acetylglucose, appears to be the hitherto unknown α-glucosidyl-β-glucoside.[68]

Polysaccharides.

Inulin.—Following the suggestion that glucose may occur as a product of hydrolysis of inulin,[69] it has been pointed out that the

[61] P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, 1931, **93**, 631; *A.*, 1400.

[62] G. Zemplén, *Ber.*, 1929, **62**, [*B*], 990; *A.*, 1929, 683; G. Zemplén and Z. S. Nagy, *ibid.*, 1930, **63**, [*B*], 368; *A.*, 1930, 456; G. Zemplén, *ibid.*, p. 1820; *A.*, 1930, 1167; G. Zemplén and A. Gerecs, *ibid.*, p. 2720; *A.*, 1931, 72.

[63] G. Zemplén, Z. Bruckner, and A. Gerecs, *ibid.*, 1931, **64**, [*B*], 744; *A.*, 716; G. Zemplén and A. Gerecs, *ibid.*, p. 1545; *A.*, 1039; G. Zemplén and Z. Bruckner, *ibid.*, p. 1852; *A.*, 1040.

[64] B. Helferich and R. Gootz, *ibid.*, p. 109; *A.*, 337.

[65] E. Pacsu, *J. Amer. Chem. Soc.*, 1931, **53**, 3099; *A.*, 1149.

[66] *Ber.*, 1926, **59**, 2230; *A.*, 1926, 1229.

[67] *J.*, 1927, 588; *A.*, 1927, 450.

[68] W. N. Haworth and W. J. Hickinbottom, *ibid.*, 1931, 2847.

[69] *Ann. Reports*, 1929, **26**, 102.

iodine value of the acid hydrolysis product of inulin is compatible with a glucose content in inulin of 5%.[70] Recent experiments of R. F. Jackson and E. McDonald, however, show that inulin from different sources (members of the family *Compositæ*) gives on hydrolysis with acid about 92% of fructose, 3% of glucose, and 5% of a group of refractory difructose anhydrides.[71] This group of disaccharides is stated to be invariably a constituent of inulin regardless of the plant from which the inulin is extracted or of the degree of purification to which the inulin is subjected. Since polysaccharides related to inulin do not yield the disaccharides, it is concluded that the latter form an integral part of the inulin molecule and are not produced by side reactions occurring during hydrolysis. The occurrence of the disaccharides in such constant proportions regardless of the source of the inulin or of its degree of purification is taken to indicate that inulin is essentially a homogeneous substance; in other words, it is composed of similarly constructed molecules, each of which contains the refractory difructose residues. The whole molecule must then contain not less than 110 hexose residues, which upon condensation and loss of 110 mols. of water, would produce a polysaccharide having the molecular weight 18,000 (compare E. Berner's value of 3,500 and H. D. K. Drew and W. N. Haworth's value of not less than about 4,000).

Three crystalline difructose anhydrides have been isolated by Jackson and McDonald which differ from the anhydrofructose isolated by J. C. Irvine and J. W. Stevenson.[72] A new difructose anhydride acetate has been derived by the action of inulinase on inulin,[73] but the corresponding difructose anhydride is not as yet known to be different from all the compounds of Jackson and McDonald.

It is suggested that inulin-bearing plants contain a series of polysaccharides of varying complexity which culminate in inulin itself.[71] As the series is ascended there is a diminishing ratio of glucose to fructose until inulin is reached. In the dahlia the development of the more complex members of the series has proceeded to such an extent that inulin is the predominating polysaccharide : a more nearly complete elimination of glucose is therefore to be expected in the dahlia inulin than in that of plants which appear to have less ability to synthesise inulin.

[70] H. Pringsheim, J. Reilly, and others, *Ber.*, 1930, **63**, [*B*], 2636; *A.*, 1930, 1562.

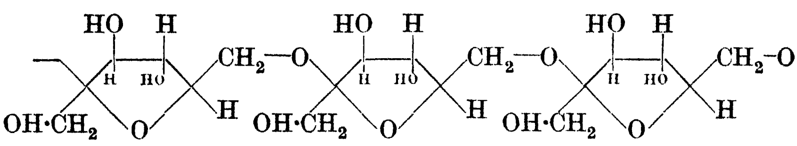
[71] *Bur. Stand. J. Res.*, 1930, **5**, 1151; 1931, **6**, 709; *A.*, 1931, 202, 827.

[72] *J. Amer. Chem. Soc.*, 1929, **51**, 2197; *A.*, 1929, 1046.

[73] H. Pringsheim and W. G. Hensel, *Ber.*, 1931, **64**, [*B*], 1431; *A.*, 941.

Lævan.—H. Hibbert and his collaborators [74] accept the view that in the growing plant glucose units which later unite to form starch and cellulose are convertible, to a considerable extent, into fructose with the resulting formation of lævulosans.[75] The wheat plant, after growing spikes, contains in its stem an alcohol-insoluble substance which yields a large amount of fructose; immature wheat grains, however, contain 6% of lævulosan and an equal percentage of starch; as maturity approaches, starch is formed in increasing quantities (50—60%) while lævulosan gradually falls to about 0·4%. The presence of these polymerised anhydrofructoses (lævulosans) is held not to be confined to any group of plants: on the contrary, their occurrence is widespread and the existence of a number of polymerides intermediate between fructose anhydride and inulin is to be expected.

Although various observers agree that bacteria can synthesise lævulosans from sucrose, and, indeed, new preparations of lævan from sucrose have been obtained by the action of *B. mesentericus* and *B. subtilis*,[74, 76] no case appears to have been recorded in which bacterial action has produced a lævulosan from glucose, as appears to occur in the plant. Lævan is apparently produced only from those sugars containing the furanose ring of fructose. The product obtained by employment of *B. mesentericus* gives a 97% yield of fructose; it also gives a triacetate differing markedly from that of inulin, and a trimethyl derivative which gives 1 : 3 : 4-trimethylfructofuranose on hydrolysis. The polysaccharide appears to be built up from the anhydro-fructofuranose unit with linkings at positions 2 and 6 of the fructose chain and is probably to be represented: [74]



The hydrolysis of lævan with 0·1*N*-oxalic acid at 65° proceeds at approximately the same rate as that of sucrose and inulin.[77]

Starch.—The view that natural starch is composed of amylopectin and amylose is not generally accepted. These substances are reported to be formed by the successive depolymerisation and

[74] H. Hibbert, R. S. Tipson, and F. Brauns, *Canadian J. Res.*, 1931, **4**, 221; *A.*, 827.

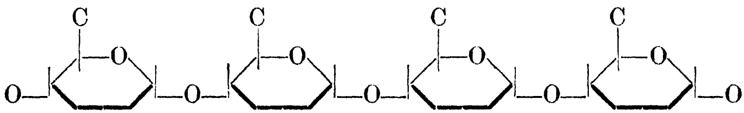
[75] H. Colin, *Bull. Soc. Chim. biol.*, 1925, **7**, 173; *A.*, 1925, i, 618.

[76] H. Hibbert and F. Brauns, *Canadian J. Res.*, 1931, **4**, 596; *A.*, 1276.

[77] H. Hibbert and E. G. V. Percival, *J. Amer. Chem. Soc.*, 1930, **52**, 3995; *A.*, 1930, 1561.

repolymerisation of natural starch, and their distinctive characteristics to arise from differences in physical character or from admixture with other substances.[78] A substance containing both phosphorus and nitrogen is reported to be present in potato- and wheat-starch, combined with the polysaccharide by means of a radical containing phosphorus; the bulk of both phosphorus and nitrogen can be extracted, the characteristics of the starch becoming somewhat changed in the process. The phosphorus content of certain potato-starch degradation products has been found to attain a value between that corresponding to a disaccharide–H_3PO_4 and a trisaccharide–H_3PO_4 aggregate.[79]

W. N. Haworth and E. G. V. Percival have shown that the biose derivable by degradation of trimethylamylose with acetyl bromide contains two glucopyranose units and conclude that the essential structure of the original polysaccharide comprises maltose residues joined to form a chain of α-glucopyranose units thus : [80]



Treatment of anhydrous maltose with hydrofluoric acid is found to give a polymeride (maltan) which is indistinguishable from a similar substance (amylan) obtainable from anhydrous potato-starch by the same treatment.[81] The isolation of various new amylosans is reported.[82]

The glycogens obtained from different sources are stated to be identical, observable distinctions being attributed to differences in the degree of polymerisation and of esterification with phosphoric acid.[83] Degradation experiments carried out with trimethyl glycogen show that glycogen is undoubtedly constituted on the same general plan as starch and consists largely of α-glucopyranose residues joined in a continuous chain as shown for starch above.[80]

[78] J. Effront, *Ann. Soc. Zymol.*, 1930, **2**, 1; *A.*, 1931, 469; S. von Náray-Szabó, *Z. physikal. Chem.*, 1930, **151**, 420; *A.*, 1931, 202. Compare M. Samec, E. Pehani, and J. Stojković, *Kolloidchem. Beih.*, 1931, **33**, 103; *A.*, 941.

[79] M. Samec and W. Bendger, *Kolloidchem. Beih.*, 1931, **33**, 95; *A.*, 941; M. Samec, S. Seliškar, and V. Zitko, *ibid.*, p. 449; *A.*, 1277.

[80] *J.*, 1931, 1342; *A.*, 941.

[81] B. Helferich, A. Starker, and O. Peters, *Annalen*, 1930, **482**, 183; *A.*, 1931, 74.

[82] H. Pringsheim, A. Wiener, and A. Weidinger, *Ber.*, 1930, **63**, [*B*], 2628; *A.*, 1930, 1561; H. Pringsheim, A. Weidinger, and P. Ohlmeyer, *ibid.*, 1931, **64**, [*B*], 2125; *A.*, 1277.

[83] K. M. Daoud and A. R. Ling, *J. Soc. Chem. Ind.*, 1931, **50**, 365, 379; *A.*, 1277.

Cellulose.—Further considerations relating to the molecular size of cellulose as deduced from viscosity measurements have been put forward by H. Staudinger and O. Schweitzer.[84] The viscosity of solutions of purified cotton in Schweitzer's reagent diminishes with time without becoming constant after four weeks, the change depending on the oxidative degradation of the macromolecules of the cellulose by copper oxide. Calculation of the molecular weight of cellulose from the viscosity of its solutions in Schweitzer's reagent shows that a more or less profound degradation of the molecule occurs according to the method of purification. The highest observed value (190,000) is for purified cotton; slight degradation accompanies mercerisation. Sulphite-cellulose and copper-silk are more appreciably affected (mol. wt. 80,000—65,000 and 35,000 respectively).

The general trustworthiness of Staudinger's procedure in applying the measurement of viscosity to the determination of the molecular weight of cellulose and its derivatives is, however, questioned by K. Hess and his collaborators,[85] who point out that the viscosimetric properties appear to be dependent on fibre purification (and accompanying disorganisation), during which foreign matter having a great influence on the viscosity is removed. Treatment of the fibre with 2% caustic soda and dilute hypochlorite solution, for example, is stated to remove a non-cellulose material localised on the outer layers, and a further component is removed by chlorine dioxide. Other workers as a result of a study of the action of dilute acids on cellulose have regarded the latter as a mixture of a crystalline phase (the source of polysaccharides) enveloped in an amorphous skin which is destroyed under more or less drastic conditions.[86]

It is contended, however, that the viscosity method is justified by the complete analogy which exists between the behaviour of these substances and that of synthetic, highly polymerised compounds.[87] With both synthetic and natural products, deviations from the Hagen–Poiseuille law become more marked with increase in molecular weight and more noticeable in concentrated than in dilute solution. They are not observed in very dilute solution (sol solution) in which the molecules have freedom of movement. It is maintained that diminution of the viscosity of cellulose solutions with increasing purification of the preparations is not due to the removal

[84] *Ber.*, 1930, **63**, [*B*], 3132; *A.*, 1931, 202.

[85] K. Hess, C. Trogus, L. Akim, and I. Sakurada, *ibid.*, 1931, **64**, [*B*], 408; *A.*, 469; K. Hess and I. Sakurada, *ibid.*, pp. 1174, 1183; *A.*, 828; compare K. H. Meyer and H. Mark, *ibid.*, p. 1999; *A.*, 1276.

[86] Bouchonnet, Jacquet, and Mathieu, *Bull. Soc. chim.*, 1930, [iv], **47**, 1265; *A.*, 1931, 202.

[87] H. Staudinger, *Ber.*, 1931, **64**, [*B*], 1688; *A.*, 1040.

of incrusting matter, but to the degradation of the sensitive macromolecules.

Formaldehyde appears to have an important influence on cellulose when applied in mercerisation operations with sulphuric acid or in the action of acetic anhydride–acetic acid mixture at 100°.[88] In the former case the fibres are protected and an enhanced affinity for substantive dyes is conferred, and in the latter the action of the acid mixture is retarded, the fibres are rendered immune to substantive dyes, and their property of linear swelling on treatment with sodium hydroxide solution is modified. It is suggested that the formaldehyde can so modify (immunise) the cellulose that the *specific* action of sodium hydroxide (cellulosate formation) is excluded. The action of the formaldehyde is conceived to result in the formation of hydroxymethyl ethers of cellulose: $>C{\cdot}OH + CH_2O \longrightarrow >C{\cdot}O{\cdot}CH_2{\cdot}OH$ or $\longrightarrow (>C{\cdot}O)_2CH_2$.

Questions relating to the adsorption of sodium hydroxide by cellulose are considered by S. Liepatov and N. Sokolova [89] and by G. Champetier.[90] The last author demonstrates by a titration method the formation of the compounds $(C_6H_{10}O_5)_2,NaOH$, $(C_6H_{10}O_5)_3,2NaOH$, $(C_6H_{10}O_5)_4,3NaOH$, and $C_6H_{10}O_5,NaOH$ in solutions containing 10 to 60% of caustic soda. The interaction of sodium with cellulose in dry liquid ammonia at its boiling point yields rapidly the monosodio-derivative ($1Na : 1C_6H_{10}O_5$), the theoretical amount of hydrogen being evolved; further reaction is then slow, but yields eventually the Na_3-derivative.[91]

It is possible by use of mixtures of phosphoric acid and nitric acid to obtain cellulose nitrate preparations (free from phosphate–nitrate esters) corresponding in nitrogen content to the pure trinitrate (14·14% N).[92] The process is accompanied by swelling of the fibres, which facilitates access of acid to the interior of the material and thus ensures uniform action. Nitration effected in this way is relatively slow, the nitric acid mercerising the cellulose before esterification commences. With other nitrating mixtures, only the nitric acid is active as an esterifying agent, but the maximum degree of nitration always falls short of the pure trinitrate.[93]

Degradation of cellulose to the triose, tetraose, and hexaose stages has been accomplished by partial hydrolysis with very concentrated

[88] M. Schenk, *Helv. Chim. Acta*, 1931, **14**, 520; *A.*, 717.

[89] *Z. anorg. Chem.*, 1930, **192**, 383; *A.*, 1930, 1562.

[90] *Compt. rend.*, 1931, **192**, 1593; *A.*, 941.

[91] P. C. Scherer, jun., and R. E. Husser, *J. Amer. Chem. Soc.*, 1931, **53**, 2344; *A.*, 1041.

[92] E. Berl and G. Rueff, *Ber.*, 1930, **63**, [*B*], 3212; *A.*, 1931, 203; *Cellulosechem.*, 1931, **12**, 53; *A.*, 606; C. Trogus, *Ber.*, 1931, **64**, [*B*], 405; *A.*, 469.

[93] R. C. Farmer, *J. Soc. Chem. Ind.*, 1931, **50**, 75; *A.*, 717.

hydrochloric acid,[94] and to the tetraose and hexaose stages by hydrolysis of appropriate acetate fractions by Zemplén's method.[95] Similarly, methylation of acetone-soluble cellulose acetate, followed by the acetolysis, deacetylation, and further methylation of the derived trimethyl cellulose, has yielded decamethyl β-methylcellotrioside and a methylated cellodextrin which is possibly a cellotetraose derivative.[96]

E. H. FARMER.

PART II.—HOMOCYCLIC DIVISION.

Tautomerism.

(Continued from *Ann. Reports*, 1929, **26**, 116.)

Prototropy.—Triad systems. The first clear case of three-carbon prototropic change in a system of the type $\overset{\oplus}{N}R_3{\cdot}CH{:}CH{\cdot}CH_2{\cdot}\overset{\oplus}{N}R'_3$, in which covalency changes beyond the limits of the system itself are structurally excluded, has been investigated by C. K. Ingold and E. Rothstein.[1] The previous case examined by these authors [2] was complicated by superimposed anionotropic changes. The isomeric bis-quaternary salts (I) and (II) have now been prepared and their individuality as separate, structural isomerides has been proved. In the presence of moderate concentrations of hydroxide or alkoxide ions, however, they undergo facile prototropic interconversion :

$$\left\{\overset{\oplus}{N}Et_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}\overset{\oplus}{N}MeEt_2\right\}\overset{\ominus}{X}_2 \rightleftharpoons \left\{\overset{\oplus}{N}Et_3{\cdot}CH{:}CH{\cdot}CH_2{\cdot}\overset{\oplus}{N}MeEt_2\right\}\overset{\ominus}{X}_2$$

(I.) (II.)

Since the hydroxy- and methoxy-derivatives of the type

$$\left\{\overset{\oplus}{N}R_3{\cdot}CH_2{\cdot}CH(OR''){\cdot}CH_2{\cdot}\overset{\oplus}{N}R'_3\right\}\overset{\ominus}{X}_2$$

($R'' = H$ or Me) could not be converted by ordinary reagents into the unsaturated derivatives, the possibility that interconversion of the latter is preceded by addition of water or alcohol to the double linking (as in the case of the di*iso*butylenes) is excluded. Finally, it should be noted that, whereas the unsymmetrical glutaconic esters often do not maintain their individuality as separate isomerides,[3] the bis-quaternary propene derivatives have separate indi-

[94] L. Zechmeister and G. Toth, *Ber.*, 1931, **64**, [*B*], 854; *A.*, 716.
[95] F. Klages, *ibid.*, p. 1193; *A.*, 827.
[96] W. N. Haworth, E. L. Hirst, and H. A. Thomas, *J.*, 1931, 824; *A.*, 941.
[1] *J.*, 1931, 1666; *A.*, 1042.
[2] *Ann. Reports*, 1929, **26**, 119.
[3] F. Feist, *Annalen*, 1922, **428**, 25, 51, 71; *A.*, 1922, i, 521, 553.

vidual existence. This is in agreement with the view[4] that the more strongly *m*-directive $\overset{\oplus}{N}R_3$ group is less effective in promoting prototropic mobility than is the more weakly *m*-directive ·COR group because, unlike the latter, it cannot provide a seat for the anionic charge.

A further example of the mobility of the indene structure[5] is furnished by the conversion of 1 : 2- into 2 : 3-diphenylindene under the influence of ethoxide ions.[6]

Important light on the conditions governing mobility and equilibrium in the αγ-diphenylmethyleneazomethine (A) and diphenylpropene (B) systems has been obtained by C. W. Shoppee.[7]

$$\text{(III.) } p\text{-}C_6H_4R\cdot CH{:}N\cdot CH_2Ph \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_6H_4R\cdot CH_2\cdot N{:}CHPh \text{ (IV.)} \quad A$$

$$\underset{\text{(V.)}}{p\text{-}C_6H_4R\cdot CH{:}C(CO_2Et)\cdot CH_2Ph} \rightleftharpoons \underset{\text{(VI.)}}{C_6H_4R\cdot CH_2\cdot C(CO_2Et){:}CHPh} \quad B$$

The following table summarises the data obtained :

R		$\overset{\oplus}{N}R_3$.	NMe_2.	OMe.	I.	(H.)	Br.	Cl.	Me.	
k_1+k_2 (hr.$^{-1}$)		—	0·054	0·557	6·82	—	7·09	7·83	0·322	A
		—	<<0·050	0·058	0·39	—	0·64	1·02	—	B
K		—	0·149	0·370	0·887	(1·0)	1·08	1·13	1·22	A
		<0·11	—	0·77	—	—	0·85	1·00	1·08	B
Equilibrium % of	III	—	87·0	73·0	53·0	(50·0)	48·0	47·0	45·0	A
	V	>90	—	56·5	—	—	54·0	50·0	48·0	B
Dipole moment of C_6H_5R, *e.s.u.* × 10^{-18}		—	+1·39	−0·80	−1·25	—	−1·51	−1·56	+0·50	

Mobility clearly runs parallel to the inductive ($-I$) effect, increasing in the order p-NMe_2<Me<OMe<Hal., and is thus obviously dependent on the ease of ionisation of the proton. On the other hand the simple view that equilibrium is controlled solely by the relative stability of the electromeric forms of the ion[8] cannot be maintained, since, interpenetrating a series of groups of the polar type $\pm I$ ($\overset{\oplus}{N}R_3$ and Me) which in themselves are correctly arranged, is a series of groups (NMe_2, OMe, Hals.) of the polar type $-I+T$, the expected order of which is completely inverted. Analysis of the system (III) $\underset{v_2}{\overset{v_1}{\rightleftharpoons}}$ ion $\underset{v_4}{\overset{v_3}{\rightleftharpoons}}$ (IV), in which the concentration of the intermediate ion is presumed to be small, shows that the equilibrium constant $K = v_1/v_2/v_3/v_4 = v_1/v_4/v_2/v_3$, that is, it is the

[4] H. Burton and C. K. Ingold, *J.*, 1928, 904; *A.*, 1928, 634.

[5] *Ann. Reports*, 1928, **25**, 119.

[6] A. García Banús and F. Calvet, *Anal. Fís. Quím.*, 1929, **27**, 49; *A.*, 1929, 688.

[7] *J.*, 1930, 968; 1931, 1225; *A.*, 1930, 912; 1931, 834.

[8] *Ann. Reports*, 1927, **24**, 106.

ratio of the ratios of the rates of ionic dissociation (facilitated by $-I$ and $-T$ and retarded only by $+I$ effects) and ionic association (facilitated by $+I$ and $+T$ and retarded only by $-I$ effects). Hence equilibrium, as opposed to mobility, involves two rate-affecting phases which partake of the nature of side-chain reactions of the opposite types. By analysis of his results the author shows that, as in cyanohydrin formation,[9] the co-existence of two antagonistic processes of control must be assumed, and, since it is shown that it is the $+T$ effect which is important, this process of duplex control must apply to a stage in which the external reagent is electron-seeking, that is, to the reassociation stage, which is thus of fundamental importance in controlling the equilibrium. Thus in the electromeric ion $C_6H_4R{\cdot}\underset{\alpha}{C}H{\cdot}\overset{\ominus}{N}{\cdot}\underset{\gamma}{C}HPh$ in which the anionic charge is distributed between C_α and C_γ, recombination of the proton will occur preferentially at C_γ either if R strongly attracts electrons ($-I$, absorption of charge on C_α) or if it strongly repels or releases them easily (strong $+I+T$; the charge developed on the carbon atom *para* to R repels electrons from C_α to C_γ); but if R repels or releases electrons only slightly (weak $+I+T$), the tendency for the aromatic ring to absorb the charge on C_α may be frustrated, causing preferential recombination at this point.

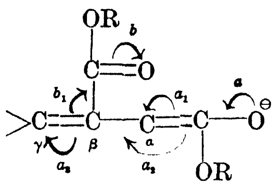
Pentad systems. In making use of data derived from the orienting effects of groups in aromatic substitution as a practical criterion of their polar effect in prototropy, care must be taken not to deduce $\pm I$ effects, which constitute a permanent *polarisation* of the molecule, by the purely mechanical inversion of $\pm T$ effects representing mainly a *polarisability* called into play only at the demand of the reagent. Thus, whereas benzene hydrogen substitution demands availability of electrons at the point of reaction and is therefore facilitated by $+I$ and $+T$ effects and retarded only by $-I$ effects, prototropy depends on the positivity of the field at the seat of ionisation and is therefore facilitated by $-I$ and $-T$ effects but retarded only by $+I$ effects. Hence, retardation of benzene hydrogen substitution does not run parallel with facilitation of prototropy unless electromeric effects of either sign are structurally impossible. As C. W. Shoppee[11] has pointed out, it does not follow that, because a β-carbethoxy-group ($-T$) tends to stabilise the βγ-phase in the system citraconic–itaconic esters,[12] a β-methyl group ($+I$) should therefore stabilise the αβ-phase. Consideration

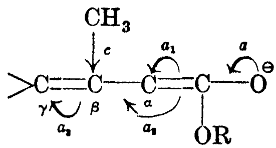
[9] A. Lapworth and R. H. F. Manske, *Ann. Reports*, 1928, **25**, 147, and ref. 27.

[11] *J.*, 1930, 968; *A.*, 1930, 912.

[12] *Ann. Reports*, 1927, **24**, 113.

of the two enolide ions in the critical stage shows that the $- T$ effect of the β-carbethoxy-group (b b_1) acts on displaceable double-bond electrons, inhibiting a_3. The $+ I$ effect of the β-methyl group (c) acts on the β-carbon, charging it negatively and directing the





electrons away from a_2 into the alternative route a; since a_3 depends on initiation from a_2 (which in turn depends on a), the $+ I$ effect (c) will also indirectly inhibit a_3. Hence, in accord with experimental results,[13] the methyl group, like the carbethoxy-group, should favour recombination of the proton at C_α with consequent stabilisation of the βγ-phase.

Further results of G. A. R. Kon and R. P. Linstead and their co-workers indicate that some factor other than the purely polar must affect the position of equilibrium in such systems.[14] The results obtained for a series of acids of the type $CHR^1R^2{\cdot}CR^3{:}CR^4{\cdot}CO_2H$ in N-sodium ethoxide at 25° are as follows : [15]

R^1R^2.	R^3.	R^4.	% αβ-Form at equilibrium.	R^1R^2.	R^3.	R^4.	% αβ-Form at equilibrium.
H_2	H	H	100	EtMe	H	H	23
H_2	Me	H	100	MeH	Et	H	21
EtH	Me	H	33	MeH	Et	Me	50
EtH	Me	Et	57	EtH	Pr^a	H	33
Me_2	H	H	approx. 10 *				

* In the case of the *iso*hexenoic acid the quantitative results are only approximate owing to the complication introduced by the addition of alcohol to the αβ-ester, which reaction is appreciably faster than the tautomeric change.

Here the qualitative effect of α-, β-, and γ-alkyl substituents follows the lines expected from theory.[16] More difficult to interpret is the effect of a substituent methyl group on the position of equilibrium in *cyclo*hexylidene- and *cyclo*pentylidene-acetic acids and the corresponding methyl ketones. Pure dry *cyclo*hexylidene- and *cyclo*-

[13] A. A. Goldberg and R. P. Linstead, *J.*, 1928, 2343; *A.*, 1928, 1214.

[14] Compare *Ann. Reports*, 1927, **24**, 112.

[15] *Ann. Reports*, 1927, **24**, 111; R. P. Linstead, *J.*, 1930, 1603 ; 1929, 2498; *A.*, 1930, 1162, 64; R. P. Linstead and J. T. W. Mann, *J.*, 1930, 2064; *A.*, 1930, 1405; G. A. R. Kon, E. Luton, R. P. Linstead, and L. G. B. Parsons, *J.*, 1931, 1411; *A.*, 934.

[16] *Ann. Reports*, 1927, **24**, 111.

hexenyl-acetic acids are interconvertible in carbon dioxide at 150°,[17] the proportion of the βγ-form (83%) in the equilibrium mixture closely approximating to that (88%) observed when equilibration is effected in sodium ethoxide. The position of equilibrium is similar in the case of the corresponding *cyclo*pentylideneacetic acid, although mobility is much greater.[18] The effect of α- and ring substituent methyl groups in the systems $(CH_2)_n$>C:CH·COR is summarised in the following table : [19]

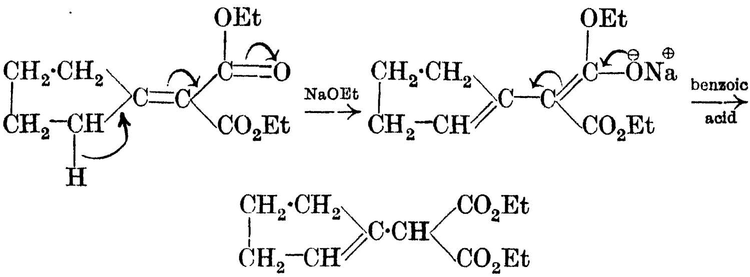
Substituent. Ring.	α-.	Acids (R = OH). % αβ-Form at equilibrium.	Mobility, $10 (k_1+k_2)$ hr.$^{-1}$.	Ketones (R = Me). % αβ-Form at equilibrium.	Mobility, $10^4 (k_1+k_2)$ min.$^{-1}$.
$n = 5$					
—	H	12	1	43	700
—	Me	32	0·0075	0	—
2-Me	H	11·5	0·15	0	—
3-Me	H	9	0·27	25	—
4-Me	H	7	0·42	13·5	600—700
$n = 4$					
—	H	14	22	84	*ca.* 3000
—	Me	38	0·58	64	3000

Thus, although, as would be expected, introduction of a methyl group in the α-position causes a marked shift in the equilibrium towards the αβ-form and a strong retardation of mobility in both acid series, the reverse effect is observed in the ketone series, similar substitution here favouring the βγ-phase, the effect on mobility being much less marked. In the *cyclo*hexene acid series nuclear methylation causes a slight displacement (4>3>2) in favour of the βγ-phase, and a similar small decrease in mobility, whilst in the corresponding ketone system introduction of a methyl group in position 2 stabilises the βγ-form to the almost complete exclusion of the αβ-form, similar substitution in position 3 or 4 exerting no pronounced effect.

The more facile mobility of the system >CH·CO·OR ⇌ >C:C(OH)·OR compared with that of its extended pentad-enol form >CH·C:C·CO·OR ⇌ >C:C·C:C(OH)·OR [20] is illustrated by results obtained by W. E. Hugh and G. A. R. Kon.[21] Ethyl *cyclo*-pentylidenemalonate is converted by sodium ethoxide into the sodio-enol. Weak acids such as benzoic are able to catalyse only

[17] R. P. Linstead, *J.*, 1930, 1603; *A.*, 1930, 1162.
[18] Compare *Ann. Reports*, 1929, **26**, 118.
[19] G. A. R. Kon and R. S. Thakur, *J.*, 1930, 2217; *A.*, 1930, 1582.
[20] *Ann. Reports*, 1927, **24**, 109.
[21] *J.*, 1930, 775; *A.*, 1930, 773.

the keto-enol change and not the less facile three-carbon tautomerism and the product contains 30—50% of the $\beta\gamma$-ester.



Contrary to the authors' previous suggestion[22] that the *cyclo*hexane ring exerts a special attraction for the double linking, similar treatment of ethyl *cyclo*hexylidenecyanoacetate causes no conversion into the $\beta\gamma$-form, nor was any such conversion observed in the case of ethyl α-cyano-β-ethylcinnamate or of ethyl α-cyano-γ-phenyl-β-methyl-Δ^{α}-butenoate. In these cases, however, the system is terminated by the combination $<^{CN}_{CO_2R}$, which is probably more effective in promoting mobility than is the group $<^{CO_2R}_{CO_2R}$.[23] The cyano-group will tend to absorb the charge on C_{α},[24] thus promoting reassociation of the proton at C_{γ} with a consequent stabilisation of the $\alpha\beta$-form. Moreover, in ethyl α-cyano-β-ethylcinnamate the phenyl group in the β-position will activate C_{γ} towards a proton[25] and thus further displace equilibrium in favour of the $\alpha\beta$-phase. R. P. Linstead[26] attributes the effect of β- and γ-phenyl substituents to an element of stability associated with conjugated systems, termed the " Thiele factor " by A. Lapworth and R. H. F. Manske.[27] The latter authors regarded this as not *necessarily* of a polar nature : R. P. Linstead asserts that it is non-polar, but the view that the phenomenon is essentially of a polar nature seems equally tenable and undoubtedly of more value in correlating a large number of experimental facts.

The Glutaconic Problem.—Some years ago a study of the addition of cyanoacetic esters to glutaconic esters led E. P. Kohler and

[22] G. A. R. Kon and E. A. Speight, *Ann. Reports*, 1927, **24**, 113.
[23] *Ibid.*, 1927, **24**, 110.
[24] J. W. Baker, K. E. Cooper, and C. K. Ingold, *ibid.*, 1928, **25**, 138.
[25] *Ibid.*, p. 146.
[26] *J.*, 1929, 2498; *A.*, 1930, 64.
[27] *J.*, 1928, 2535; *A.*, 1928, 1245.

G. H. Reid [28] to the conclusion that these reactions proceed as would be expected with αβ-unsaturated esters, the results lending no support to the conception of a " normal " form of the glutaconic esters having a symmetrical formula and a capacity for addition in the 1 : 3-positions.

The whole subject is now being re-examined in the South Kensington laboratories.[29] The resolution of " normal " αγ-dimethylglutaconic acid into optically active forms [30] points directly to the unsymmetrical structure $CO_2H\cdot CMe{:}CH\cdot CHMe\cdot CO_2H$. A careful examination of the tautomerism of some cyanoglutaconic esters by G. A. R. Kon and H. R. Nanji has led to the isolation of both the Δ^{α}- and the Δ^{β}-isomeride of ethyl α-cyano-βγ-dimethylglutaconate,

$$CO_2Et\cdot C(CN){:}CMe\cdot CHMe\cdot CO_2Et$$
$$\text{and } CO_2Et\cdot CH(CN)\cdot CMe{:}CMe\cdot CO_2Et$$

and the proof that both the " normal " and the labile form described before [31] consist of the equilibrium mixture arising from the catalytic action of sodium ethoxide on the Δ^{α}-ester.

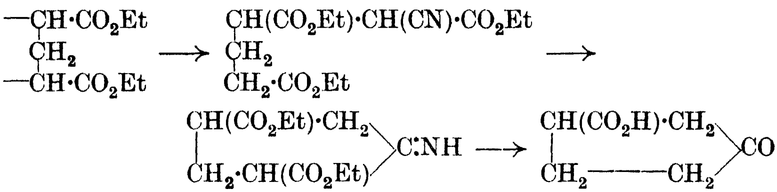
These results are in fact adequately explained without the special assumption of a " normal " form, and the view that the isomerism of the glutaconic acids and their derivatives is due to the occurrence of three-carbon tautomerism together with *cis-trans* isomerism will, no doubt, now be generally accepted. This was substantially the contention of F. Feist,[32] who, however, seems to have overemphasised the single factor of *cis-trans* isomerism, regarding the three-carbon systems as always dynamic. In actual fact, where a crystalline substance is isolated, a static formula must be assigned to it, and both structural and steric isomerism may be expected to occur.

In an investigation of some substituted glutaconic esters from this point of view G. A. R. Kon and E. M. Watson find that two forms of the ester of α-benzyl-β-methylglutaconic acid arise, shown by ozonolysis to be structurally isomeric. These are found to be the *cis*-αβ- and the *trans*-βγ-isomeride : the remaining stereoisomerides (*trans*-αβ and *cis*-βγ) have not yet been isolated.[33]

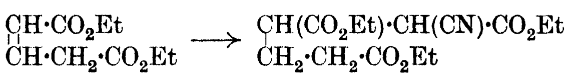
Two anomalous cases still remain which have hitherto been regarded as evidence of the " normal " form of glutaconic acids.

[28] *J. Amer. Chem. Soc.*, 1925, **47**, 2803; *A.*, 1926, 48.
[29] *J.*, 1931, 1011.
[30] T. H. McCombs, J. Packer, and J. F. Thorpe, *ibid.*, p. 547; *A.*, 604.
[31] *J.*, 1931, 560; *A.*, 608; compare N. Bland and J. F. Thorpe, *J.*, 1912, **101**, 871; *Ann. Reports*, 1912, **9**, 85—89.
[32] *Loc. cit.*, ref. 3.
[33] *J.*, 1932, 1.

The first of these is the isolation,[34] from the products of the reaction of ethyl sodiocyanoacetate with ethyl β-hydroxyglutarate (which under the experimental conditions gives " nascent " ethyl glutaconate), in addition to the expected 1 : 2-additive product, of a small proportion of ethyl *cyclo*pentanone-2 : 4-dicarboxylate (hydrolysed to *cyclo*pentanone-3-carboxylic acid).[35] This must be produced by cyclisation of ethyl α-cyano-β-carbethoxyadipate apparently formed by 1 : 3-addition :



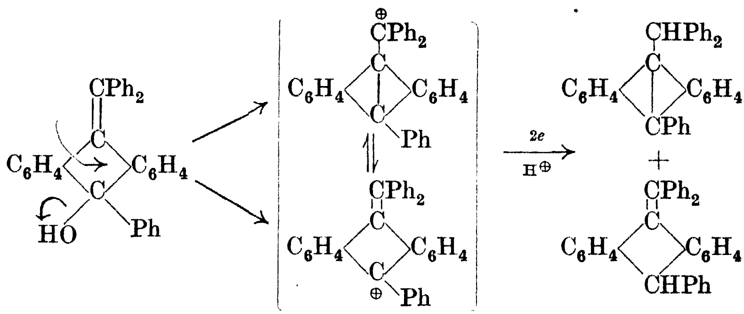
It should be noted, however, that in ethyl glutaconate a strongly polar carbethoxy-group is present on each side of the double linking, with a methylene group intervening on one side only. Hence, just as the addition of iodine chloride to a double bond occurs in both senses, only the major product being in accord with Markovnikov's rule,[36] the by-product in the above reaction may possibly be due, not to 1 : 3-addition, but to reversed 1 : 2-addition :



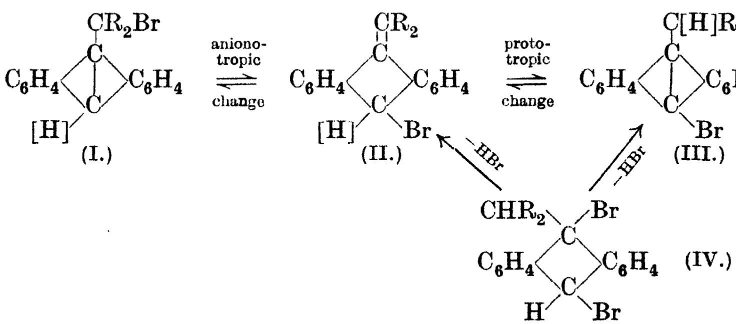
If this explanation is correct, there only remains the second anomaly, namely, the reported isomeric forms of the ester of 3-methyl*cyclo*propene-1 : 2-dicarboxylic acid.[37] Some explanation of this will no doubt soon be found.

Transannular Tautomerism.—The isolation of two transannular (also termed transannelar) isomeric hydrocarbons is described by E. Bergmann.[38] Benzhydrylideneanthrone is converted by phenylmagnesium bromide into 10-hydroxy-10-phenyl-9-benzhydrylidene-9 : 10-dihydroanthracene, which is reduced by sodium formate and formic acid to a mixture of 10-phenyl-9-benzhydrylidene-9 : 10-dihydroanthracene and 10-phenyl-9-benzhydrylanthracene. The latter is converted into the former through its sodium derivative.

[34] C. K. Ingold and J. F. Thorpe, *J.*, 1921, **119**, 492.
[35] F. W. Kay and W. H. Perkin, *J.*, 1906, **89**, 1645.
[36] A. Michael, *J. pr. Chem.*, 1899, **60**, 450; *A.*, 1900, i, 321.
[37] *Ann. Reports*, 1923, **20**, 107—110.
[38] *Ber.*, 1930, **63**, [*B*], 1037; *A.*, 1930, 902.



The possibility of both prototropic and anionotropic changes in 9-arylidene-9 : 10-dihydroanthracene derivatives of type (II) must be borne in mind [39] in the interpretation of the results obtained by bromination of 9-alkyl- or 9-aryl-anthracenes, the investigation of which has been continued by E. de Barry Barnett and his collaborators. It will be noticed that the intermediate dibromide (IV), which is presumably the initial product in the bromination, can pass directly by elimination of hydrogen bromide into derivatives of type (II) or (III), and, when such derivatives are formed, conditions governing the mobility and equilibrium of *prototropic* systems are obviously involved. Derivatives of type (I), however, cannot



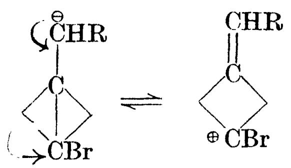
be thus directly obtained and their formation indicates that conditions governing anionotropic changes must be considered. In this respect the effect of α-chlorine substitution on the bromination of 9-substituted anthracenes is instructive. Bromination of 4-chloro-9-benzyl- and 4 : 5-dichloro-9-methyl-anthracene affords, respectively, 4-chloro-ω-bromo-9-benzyl- and 4 : 5-dichloro-9-bromomethyl-anthracene [40] (both of type I), which are the stable forms anticipated in the anionotropic system involved.[39]

[39] *Ann. Reports*, 1928, **25**, 130.
[40] J. W. Cook, *J.*, 1928, 2802; *A.*, 1928, 1365.

The following table summarises the effect of nuclear substitution on the relative proportions of derivatives of types (II) and (III) in the bromination of various 9-arylanthracenes :

Nuclear substituent.	R_2.	Predominant form of bromination product.
Unsubstituted [41]	Ph, H	III
2-Chloro [42]	Ph, H	III
1-Chloro [43]	Ph, H	70% (II) 30% (III)
1 : 8- or 1 : 5-Dichloro [44]	Ph, H	II
Unsubstituted [45]	p-Cl·C_6H_4·, H	III
1 : 5-Dichloro [45]	p-Cl·C_6H_4·, H	II
2 : 3-Dimethyl [46]	Ph, H	III
1 : 4- ,, [47]	Ph, H	II

In these cases prototropic change is involved and the effect of nuclear chlorine-substitution is readily explained by the — I effect of the chlorophenyl nucleus, which, by withdrawing electrons from the central nucleus, will tend to stabilise the negative charge of the electromeric anion on the nuclear atom C_{10} with the resultant



Ion-Type (III). Ion-Type (II).

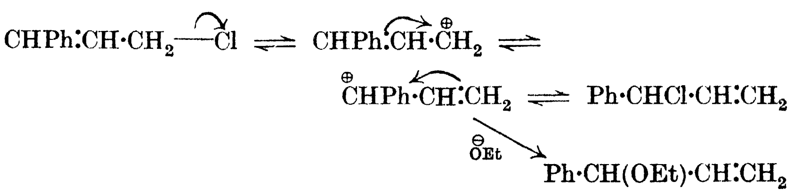
preferential (1-chloro-) or exclusive (1 : 5- or 1 : 8-dichloro-) formation of derivatives of type (II). The case of 1 : 4-dimethyl substitution is, from this point of view, anomalous.[48]

Anionotropy.—A study of further examples confirms the conclusions previously reported [49] relating to the factors affecting the *mobility* of anionotropic systems. Thus in boiling acetic anhydride both methylvinylcarbinyl and crotyl trichloroacetates afford the same equilibrium mixture containing 55% of the former, whilst α-m-4-xylylallyl alcohol is converted into 2 : 4-dimethylcinnamyl alcohol by acetylation and subsequent hydrolysis.[50]

[41] J. W. Cook, *J.*, 1926, 2161; *A.*, 1926, 1131.
[42] E. de B. Barnett and J. L. Wiltshire, *J.*, 1928, 1822; *A.*, 1928, 995.
[43] J. W. Cook, *J.*, 1928, 2802; *A.*, 1928, 1365.
[44] E. de B. Barnett, N. F. Goodway, and J. L. Wiltshire, *Ber.*, 1930, **63**, [*B*], 472; *A.*, 1930, 465.
[45] E. de B. Barnett and J. L. Wiltshire, *ibid.*, 1929, **62**, [*B*], 3072; *A.*, 1930, 202.
[46] E. de B. Barnett and F. C. Harrison, *ibid.*, 1931, **64**, [*B*], 535; *A.*, 612.
[47] E. de B. Barnett and L. A. Low, *ibid.*, p. 49; *A.*, 341.
[48] Compare E. de B. Barnett and C. L. Hewett, *ibid.*, p. 1572; *A.*, 1058.
[49] *Ann. Reports*, 1928, **25**, 127.
[50] H. Burton, *J.*, 1930, 248; *A.*, 1930, 450.

The increased activation of a three-carbon anionotropic system by polynuclear aryl groups is illustrated by the conversion of α- and β-naphthylvinylcarbinols into γ-1- and γ-2-naphthylallyl *p*-nitrobenzoates, respectively, by the action of *p*-nitrobenzoyl chloride and pyridine, under which conditions the corresponding phenyl derivatives each give the ester of the original alcohol.[51]

The position of *equilibrium* of such systems, however, is largely affected by experimental conditions. Thus, whereas the action of anhydrous hydrogen halides on either cinnamyl or α-phenylallyl alcohol gives only cinnamyl halides, treatment of cinnamyl chloride with 70% aqueous-alcoholic potassium hydroxide affords 20—25%, and with silver oxide in absolute alcohol, 35—45%, of α-phenylallyl ethyl ether.[52]



The formation of the ether is readily explained by the greater co-ordinating power of the ethoxide, relative to that of the chloride ion. In the halides recombination of the anion occurs exclusively in the γ-position to the phenyl group, but the ethoxide ion combines in the α-position, indicating a considerable displacement of the equilibrium under these conditions in favour of the other electromeric form of the kation.

Differences in experimental conditions also explain C. Prévost's [53] failure to confirm H. Burton's results (above) on the interconversion of crotyl and methylvinylcarbinyl esters, since the low dielectric constant of the solvents (toluene and trichloroacetic acid), the lower temperatures, and the shorter periods of heating employed may prevent a system of such small mobility from attaining complete equilibrium.

Aromatic Substitution.

(Continued from *Ann. Reports*, 1930, **27**, 130.)

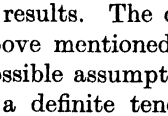
General Theory. Dynamics of Aromatic Substitution.—The modern electronic view of aromatic substitution has been elaborated almost exclusively from observations of the proportions of

[51] H. Burton, *J.*, 1931, 759; *A.*, 723.

[52] J. Meisenheimer and J. Link, *Annalen*, 1930, **479**, 211; *A.*, 1930, 769: compare H. Gilman and S. A. Harris, *J. Amer. Chem. Soc*, 1931, **53**, 3541; *A.*, 1290.

[53] *Bull. Soc. chim.*, 1931, [iv], **49**, 261; *A.*, 601.

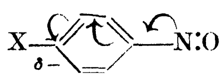
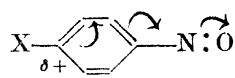
isomerides simultaneously formed, but four years ago the importance was emphasized of considering not only the proportions of isomerides, but also the relative velocities of substitution, and preliminary data of the latter kind were reported.[54] Accurate measurements of the reduced velocity of substitution of toluene relative to benzene have now been furnished by C. K. Ingold, A. Lapworth, E. Rothstein, and D. Ward,[55] and the effect of certain modifications in experimental conditions has been ascertained. Under standard conditions (nitration by acetyl nitrate at 30°) the values of the partial rate factor F (previously designated as the coefficient of activation, *viz.*, the factor by which the introduction of the directing group increases the probability of substitution at a given nuclear carbon atom) for the *o*-, *m*-, and *p*-positions are respectively 40, 3·0, and 51. Hence, in agreement with the earlier findings of C. K. Ingold and F. R. Shaw,[54] the methyl group not only causes a large increase in *op*-reactivity but also a small increase in *m*-reactivity. Alteration of the reagent and solvent to nitric acid in nitromethane gave identical values for F, whilst changing the temperature to 0° resulted in a slightly higher reduced velocity and generally higher coefficients of activation.

It was shown by A. E. Bradfield and B. Jones [56] that in *o*- and *p*-substituted alkoxybenzenes the two substituents contribute characteristically and additively to the logarithm of the velocity of nuclear halogenation, on the assumption that in the equation for the critical energy increment $k = \alpha e^{-E/RT}$, variations in k are due entirely to variations in E, α remaining constant. The halogenation of a further series of phenyl ethers and of *p*-tolyl ethers of the general formula  at 20° and 35° has now been studied.[57] There is little difference between the rates of chlorination of corresponding chloro- and bromo-ethers, and the group contributions for the new phenyl ethers examined are in agreement with the earlier results. The data also serve to confirm the original hypothesis above mentioned and to discredit three other (more complicated) possible assumptions. At the same time some of the figures reveal a definite tendency to departure from the simple additive relation in directive effects of groups. Thus the relative effects in the series of tolyl ethers agree with the results for phenyl ethers when X is NO_2 but not when X is a halogen;

[54] *Ann. Reports*, 1927, **24**, 152.
[55] *J.*, 1931, 1959; *A.*, 1405.
[56] *Ann. Reports*, 1928, **25**, 143.
[57] A. E. Bradfield and B. Jones, *J.*, 1931, 2903; A. E. Bradfield, W. O. Jones, and F. Spencer, *ibid.*, p. 2907.

and in general the relative directive effects are 5—15% lower in the tolyl ether series than for the corresponding phenyl ethers.

The conclusion that the nitroso-group is *m*-directive [58] was based mainly on the slow velocity of bromination and absence of *p*-substitution of nitrosobenzene in acetic acid, in which solvent it is not associated, and on the reaction of the bromine in *p*- but not in *m*-bromonitrosobenzene with silver nitrate in acetic acid. Caution should be observed, however, in accepting this conclusion, since R. J. W. Le Fèvre [59] has found that *p*-bromonitrosobenzene reacts with silver nitrate under conditions in which even picryl bromide (activation by three nitro-groups) is unattacked. Moreover, nitrosobenzene can be mono-*p*-brominated in benzene, a solvent in which it is also unimolecular. The most satisfactory view of the properties of the nitroso-group would seem to be that it is capable of electromeric effects of either sign,[60] aromatic hydrogen substitution or replacement of halogen being controlled by displacements of type (I), whereas hydrolytic reactions (*e.g.*, the hydrolysis of *p*-nitrosodimethylaniline) are initiated by those of type (II).

(I.)   (II.)

Ionogenic Systems.—By analogy with Schiff's bases, which have previously been proved [61] to exist, in concentrated sulphuric acid solution, as salts of the type $\overset{\oplus}{\overbrace{\text{PhCH:NHAr}}}\}\overset{\ominus}{\text{X}}$, J. W. Baker [62] has suggested that the intensely coloured solutions formed by benzaldehyde and acetophenone in the same medium are due to the formation of oxonium salts of the type $\overset{\oplus}{\overbrace{\text{PhCR:OH}}}\}\overset{\ominus}{\text{HSO}_4}$, the ions of which are in equilibrium with the colourless, pseudo-salt form. Partition (between sulphuric acid and ligroin) and colorimetric data indicate that the equilibria

$$\underbrace{\text{PhCR:O}}_{\text{soluble}} + \text{HO}\cdot\text{SO}_3\text{H} \rightleftharpoons \text{PhCR(OH)}\cdot\text{O}\cdot\text{SO}_3\text{H} \rightleftharpoons \text{O}\cdot\overset{\ominus}{\text{S}}\text{O}_3\text{H} + \overset{\oplus}{\overbrace{\text{PhCR:OH}}}$$

←———— colourless ————→ coloured

soluble ←———— insoluble in ligroin ————→

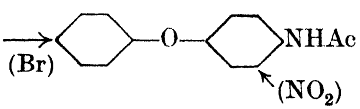
are displaced largely towards the right even in 80% sulphuric acid. As in the case of Schiff's bases, the distribution of the positive charge on the carbonium-oxonium kation causes a considerable increase in the proportion of *m*-nitration observed under these

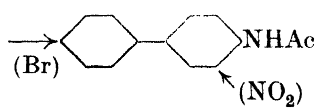
58 *Ann. Reports*, 1930, **27**, 130.
59 *J.*, 1931, 810; *A.*, 945: but compare D. L. Hammick, *ibid.*, p. 3105.
60 R. Robinson, *Chem. and Ind.*, 1925, **44**, 456.
61 *Ann. Reports*, 1930, **27**, 136. 62 *J.*, 1931, 307; *A.* 486.

conditions.[63] Thus in 7·3% oleum, benzaldehyde and acetophenone afford 90·8 and 90·0% of the *m*-isomeride, respectively. This proportion decreases gradually as the concentration of the sulphuric anhydride is diminished until in 80% sulphuric acid the values are 83·9 and 83·1%, and in nitric acid (*d* 1·53) alone, 72·1 and 70%, respectively. Moreover, in all cases, addition of ammonium sulphate to the sulphuric acid nitrating medium causes a depression in the amount of *m*-isomeride formed, comparable both in magnitude and in type with that observed in the case of Schiff's bases, an indication that substitution occurs mainly through the kation of the oxonium salt.

Miscellaneous.—Further examples of the effect of experimental conditions in altering the proportion of isomerides formed have been recorded. Thus, although the occurrence of a large amount (85%) of *m*-substitution when phenylboric acid is nitrated with nitric acid (*d* 1·53) has been confirmed, in acetic anhydride a 65% yield of a mixture containing 95% of *o*- and 5% of *p*-nitrophenylboric acid is obtained.[64] Pending further investigation, this result suggests that the explanation of the *m*-directive power previously given[65] should be accepted with reserve.

That the nature of the substituting reagent also affects the position of substitution is illustrated by results obtained with diphenyl derivatives and diphenyl ethers. Thus *p*-acetamidodiphenyl ether is nitrated [66] and brominated [67] respectively in the positions shown :





these results forming a parallel with those obtained by J. Kenyon and P. H. Robinson [68] in the case of 4-acetamidodiphenyl. Nitration of 4-acetamido-4′-methoxydiphenyl ether also occurs in position 3, whilst *p*-methoxydiphenyl ether is brominated in the 4′-position. Similar differences are found by F. Bell [69] in the case of 3-bromo-4-*p*-toluenesulponamidodiphenyl, which is nitrated in position 5, but brominated in position 4′. The explanation of these results may lie in the lower degree but higher frequency of activation in position 4′ than in position 3 or 5,[70] so that the more ener-

[63] J. W. Baker and W. G. Moffitt, *J.*, 1931, 314; *A.*, 485.
[64] W. Seaman and J. R. Johnson, *J. Amer. Chem. Soc.*, 1931, **53**, 711; *A.*, 502.
[65] *Ann. Reports*, 1930, **27**, 133.
[66] M. Oesterlin, *Monatsh.*, 1931, **57**, 31; *A.*, 479.
[67] *Ann. Reports*, 1930, **27**, 142.
[68] *J.*, 1926, 3050; *A.*, 1927, 142. [69] *J.*, 1931, 2338; *A.*, 1284.
[70] A. Lapworth and R. Robinson, *Mem. Manchester Phil. Soc.*, 1927, **72**, 43; *A.*, 1927, 546.

getically negative-centre seeking reagent, bromine, enters position 4′. When bromination of 3-bromo-4-*p*-toluenesulphonamidodiphenyl is carried out in pyridine, the activating power of the *p*-toluenesulphonamido-group is increased by removal of its incipiently ionised hydrogen by salt formation, and the second bromine enters at position 5.

In conclusion, attention may be directed to investigations on the action of bromine on phenols,[71] and on the chlorination of iodophenols.[72]

Polycyclic Aromatic Compounds.

No systematic report on this subject has been made for several years, but limitation of space restricts the following summary to a brief outline of a few of the more important lines of general development. Attention may be directed to the monograph on "Higher Coal Tar Hydrocarbons" by A. E. Everest which gives an account of the chemistry of higher polycyclic aromatic hydrocarbons up to the end of 1926.

Naphthalene.—Alkylnaphthalenes. After removal of 1 : 6-, 2 : 6-, and 2 : 7-dimethylnaphthalenes from low-temperature coal tar, 2 : 3-dimethylnaphthalene has been isolated as its 6-sulphonic acid and converted into various derivatives.[73]

The α-directive catalytic influence of mercury in the sulphonation of naphthalene finds a parallel in the exclusive formation of β-derivatives when tetrahydronaphthalene is condensed with alkyl bromides or acyl chlorides in the presence of aluminium halides, other metallic halides affording mixtures of α- and β-derivatives.[74] Catalytic dehydrogenation of the products affords 2-alkylnaphthalenes and β-naphthyl ketones, respectively. Similar condensation of *tert.*-butyl chloride with naphthalene itself, however, gives a mixture of di-*tert.*-butylnaphthalenes.[75]

By modifications of the general method involving ring-closure of substituted γ-phenylbutyryl chlorides with aluminium chloride, followed by reduction and subsequent catalytic dehydrogenation, I. M. Heilbron and his co-workers have synthesised 1-methyl-5-, -6-, and -7-ethylnaphthalene,[76] and 2 : 3 : 5-, 1 : 3 : 5-, and 1 : 3 : 8-trimethylnaphthalene.[77] Neither the 1 : 3 : 5- nor the 1 : 3 : 8-derivative is identical with the trimethylnaphthalene obtained by dehydrogenation of tetra*cyclo*squalene.[78] Since the oxidation products

[71] G. Heller (with others), *J. pr. chem.*, 1931, [ii], **129**, 211; *A.*, 477.
[72] S. Buchan and H. McCombie, *J.*, 1931, 137; *A.*, 345.
[73] O. Kruber, *Ber.*, 1929, **62**, [*B*], 3044; *A.*, 1930, 202.
[74] A. Barbot, *Bull. Soc. chim.*, 1930, [iv], **47**, 1314; *A.*, 208.
[75] W. Gump, *J. Amer. Chem. Soc.*, 1931, **53**, 380; *A.*, 341.
[76] J. Harvey, I. M. Heilbron, and D. G. Wilkinson, *J.*, 1930, 423; *A.*, 1930, 593.
[77] D. G. Wilkinson, *J.*, 1931, 1333; *A.*, 948.
[78] *Ann. Reports*, 1927, **24**, 128.

of the latter could arise only from the 1 : 3 : 8- or the 1 : 2 : 5-trimethyl derivative, it must be the latter,[79] a conclusion subsequently confirmed by the synthesis of this hydrocarbon by L. Ruzicka and J. R. Hosking.[80] The same hydrocarbon results from the catalytic dehydrogenation of Congo copal oil.[81] The syntheses of 1 : 5-, 1 : 8-,[82] and 2 : 8-[83]dimethylnaphthalene have also been effected. The conversion of 2-methylnaphthalenes into benzanthracenes is discussed on p. 126.

Substitution of naphthalene derivatives. The problem of orientation in the naphthalene nucleus is complex from both the experimental and the theoretical point of view. The study of this field on modern lines has not yet made much progress, but a few recent investigations may be mentioned.

The nitration of α-chloro- or α-bromo-naphthalene occurs successively at positions 4, 5, and 8, and of α-alkoxynaphthalenes at positions 2, 4, and 5.[85] Nitration of 2-chloro-, bromo-, or alkoxynaphthalene yields the 1 : 6 : 8-trinitro-derivative.[86] The halogen atom in such compounds is readily replaced by positive-centre seeking groups such as OH, OR, and S. The influence of a nitro-group in producing high reactivity in a halogen atom is found by J. Salkind [87] not to extend from one ring to the other of the naphthalene nucleus. On the other hand it is well known that in halogen substitution a group often deactivates one nucleus as a whole relative to the other.[84]

Chlorosulphonic acid converts 1-methylnaphthalene into the 4-sulphonic acid,[88] although 2-methylnaphthalene is stated to give the 8-sulphonic acid.[89] Further nitration of a mixture of 4- and 5-nitro-1-methylnaphthalene gives the 4 : 5-dinitro-derivative, whilst the presence of some 2 : 4-dinitro-compound is indicated by the formation of 2-nitro-4-amino- and 4-nitro-2-amino-1-methylnaphthalene on reduction.[90]

79 I. M. Heilbron and D. G. Wilkinson, *J.*, 1930, 2546; *A.*, 80.

80 *Helv. Chim. Acta*, 1930, **13**, 1402; *A.*, 231.

81 L. Wertenburg and J. P. Wibaut, *Rec. trav. chim.*, 1931, **50**, 188; *A.*, 484.

82 V. Veselý and F. Štursa, *Coll. Czech. Chem. Comm.*, 1931, **3**, 430; *A.*, 1282.

83 V. Veselý and A. Medvedeva, *ibid.*, p. 440; *A.*, 1282.

84 *Ann. Reports*, 1926, **23**, 134; 1930, **27**, 140.

85 H. W. Talen, *Rec. trav. chim.*, 1928, **47**, 329, 346; *A.*, 1928, 405.

86 E. J. van der Kam, *ibid.*, 1926, **45**, 564, 722; *A.*, 1926, 1029, 1239.

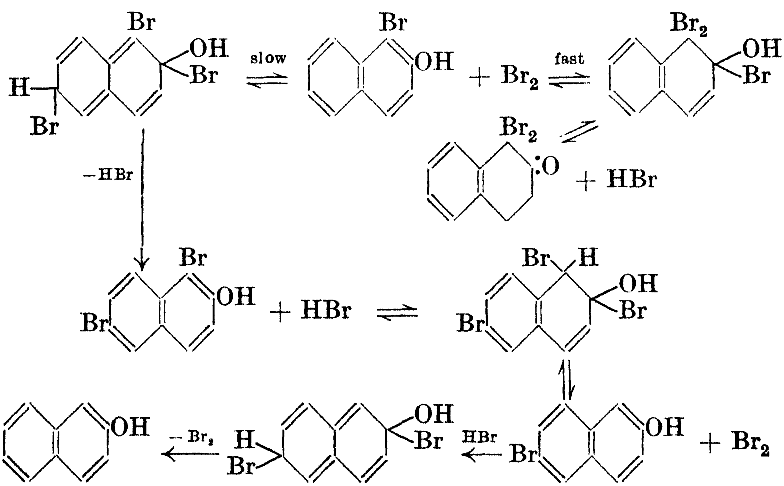
87 *Ber.*, 1931, **64**, [*B*], 289; *A.*, 474; compare *Ann. Reports*, 1929, **26**, 132.

88 R. E. Steiger, *Helv. Chim. Acta*, 1930, **13**, 173; *A.*, 1930, 593.

89 K. Dziewoński and A. Wulffsohn, *Bull. Acad. Polonaise*, 1929, *A*, 143; *A.*, 1929, 803.

90 V. Veselý, F. Štursa, H. Olejniček, and E. Rein, *Coll. Czech. Chem. Comm.*, 1929, **1**, 493; 1930, **2**, 145; *A.*, 1929, 1288; 1930, 593.

An investigation of the bromination of β-naphthol by K. Fries and K. Schimmelschmidt[91] has explained various discrepancies in the literature. Such bromination affords, successively, the 1-mono-, 1 : 6-di-, and 1 : 4 : 6-tri-bromo-derivatives.[92] The tetra-bromo-β-naphthols, formed by bromination in acetic acid, consist of the 1 : 3 : 4 : 6-, 1 : 3 : 5 : 6-, and 1 : 3 : 6 : 8-derivatives, the last two compounds not being formed by simple substitution processes. The reaction $C_{10}H_7 \cdot OH(\beta) + Br_2 \rightleftharpoons C_{10}H_6Br \cdot OH + HBr$ is reversible, since treatment of 1-bromo-β-naphthol with a saturated solution of hydrogen bromide in acetic acid in the presence of potassium iodide (to remove bromine) affords β-naphthol. The course of bromination is largely influenced by the conversion of β-naphthol into quinonoid forms. Bromination of keto-bromides (the formation of which is favoured by the addition of sodium acetate to remove hydrogen bromide) and subsequent reduction of the products gives rise to different derivatives from those obtained when bromo-β-naphthols are brominated. Thus 1 : 3 : 6- and not 1 : 4 : 6-tribromo-β-naphthol is produced when 1 : 1-dibromo-2-keto-1 : 2-dihydronaphthalene is brominated and the product reduced. The mechanism of the formation of the 1 : 6-dibromo-compound and its successive reconversion into the 6-bromo-derivative and into β-naphthol is indicated in the following scheme :

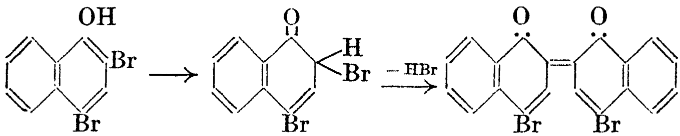


Similar ketonisation of 2 : 4-dibromo-α-naphthol is suggested as

[91] *Annalen*, 1930, **484**, 245; *A.*, 215.

[92] Compare H. Franzen and G. Stauble, *J. pr. Chem.*, 1921, [ii], **103**, 352; *A.*, **1922**, i, 450.

the mechanism of its conversion into the indigotin type of derivative (I) under the influence of alkali: [93]



(I.)

Bromination of 1 : 5-dihydroxynaphthalene yields the 2 : 6-dibromo-derivative, which, on oxidation, affords 2 : 6-dibromo-5-hydroxy-1 : 4-naphthaquinone, only one of the rings being converted into the quinonoid form.[94]

Naphthalene-azo- and -diazo-compounds. An interesting new reaction of various aryl diazosulphonates of β-naphthol-1-sulphonic acid has been investigated by F. M. Rowe and his collaborators.[95] Whilst acidification of a solution of 4′-nitrobenzene-2-naphthol-1-diazosulphonate (II) in a molecular quantity of sodium hydroxide gives a quantitative yield of Para-red (*p*-nitrobenzeneazo-β-naphthol), addition of the diazosulphonate in sodium carbonate solution to an excess of sodium hydroxide and subsequent acidification gives only a trace of Para-red, the main product being the sodium salt of 3-(4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic-1-sulphonic acid. This compound, to which structure (V) is provisionally assigned, is converted by boiling hydrochloric acid into the corresponding 1-hydroxy-derivative (VI).

Although the condensation products of diazotised *p*-nitroaniline with 1-halogeno- or 1-methyl-β-naphthol are true diazo-oxides,[96] the initial stage in the above reaction is the formation, not of a diazo-oxide (XII) as postulated by H. T. Bucherer,[97] but of sodium 4′-nitrobenzene-1-azo-β-naphthaquinone-1-sulphonate (III), ring fission and subsequent cyclisation of the acid (IV) giving the dihydrophthalazine derivative (V). The corresponding hydroxy-compound (VI) is reduced to 1-hydroxy-3-(4′-aminophenyl)tetrahydrophthalazine-4-acetic acid (VII). The possible alternative *iso*quinoline structure (XIII) is shown to be untenable by a comparison of its properties with those of *N*-4′-nitrophenylamino*iso*-

[93] R. Willstätter and L. Schuler, *Ber.*, 1928, **61**, [*B*], 362; compare S. Goldschmidt and H. Wessbecher, *ibid.*, p. 372; *A.*, 1928, 408, 409.

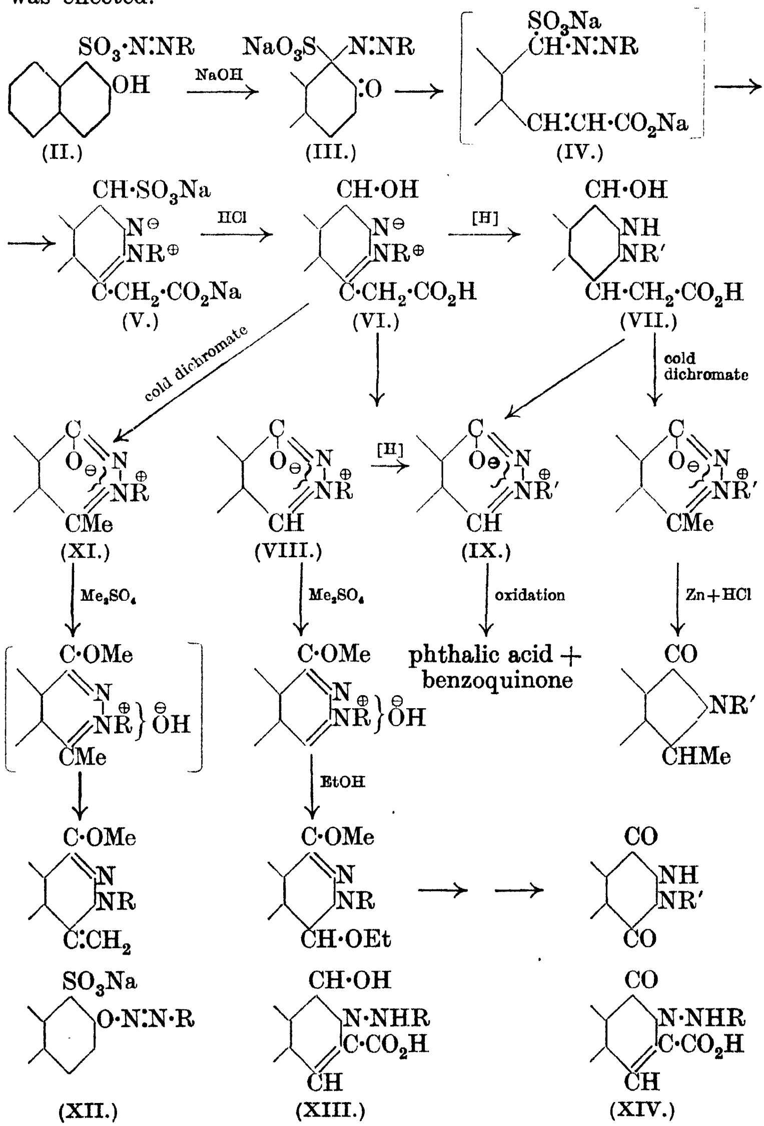
[94] A. S. Wheeler and D. R. Ergle, *J. Amer. Chem. Soc.*, 1930, **52**, 4872; *A.*, 217.

[95] F. M. Rowe, E. Levin, A. C. Burns, J. S. H. Davies, and W. Tepper, *J.*, 1926, 690; *A.*, 1926, 625.

[96] F. M. Rowe and A. T. Peters, *J.*, 1931, 1065; *A.*, 835; compare J. Pollak and E. Gebauer-Fülnegg, *Monatsh.*, 1928, **50**, 310; *A.*, 1929, 58.

[97] *Ber.*, 1909, **42**, 47; *A.*, 1909, i, 193; H. T. Bucherer and C. Tama, *J. pr. Chem.*, 1930, **127**, 39; *A.*, 1930, 1280; compare A. Wahl and R. Lantz, *Bull. Soc. chim.*, 1923, **33**, 97; *A.*, 1923, i, 209.

carbostyril-3-carboxylic acid (XIV), a rational synthesis of which was effected.



(R = p-$NO_2 \cdot C_6H_4 \cdot$; R′ = p-$NH_2 \cdot C_6H_4 \cdot$)

Boiling with dilute mineral acids converts (VI), with elimination of acetic acid, into 4′-nitro-3-phenylphthalaz-1-one[98] (VIII).

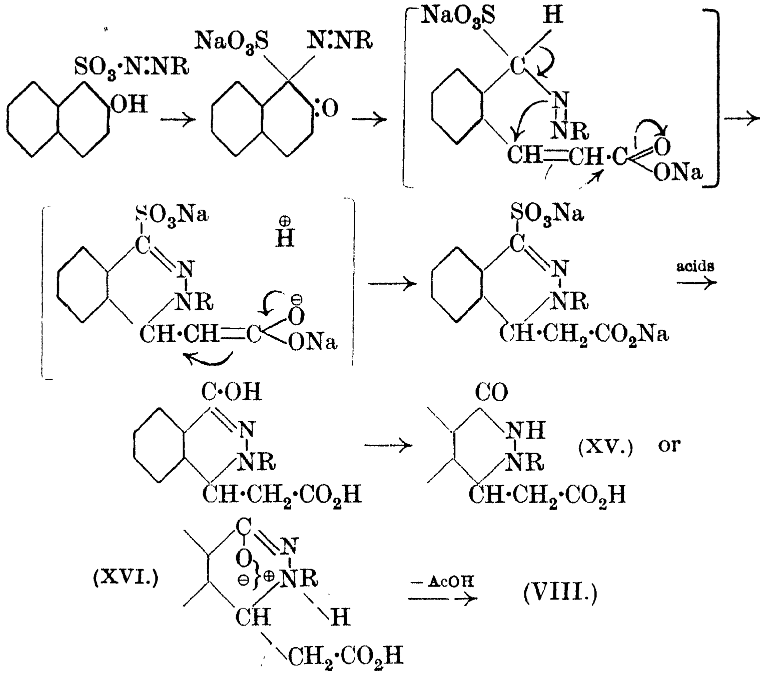
[98] F. M. Rowe and E. Levin, *J.*, 1928, 2550; *A.*, 1928, 1262.

The latter, in agreement with the betaine structure assigned, exhibits both acidic and basic properties and is reduced to the corresponding amino-compound (IX), similarly obtained from (VII). The isomeric 4′-nitro-3-phenylphthalaz-4-one, which was synthesised for comparison, is insoluble in alkali and does not yield salts with mineral acids. On the other hand, cold acid potassium dichromate merely decarboxylates the acetic acid side chain in (VI), giving 4′-nitro-3-phenyl-4-methylphthalaz-1-one (XI).[99]

A similar series of derivatives is obtained from 3′-nitrobenzene-[1] and 2′ : 6′-dichloro- and 2′ : 6′-dibromo-4′-nitrobenzene-2-naphthol-1-diazosulphonates,[2] but it is perhaps significant that in this series of decreasing — *I* and increasing + *T* effects there is an increasing tendency towards the formation of the corresponding benzeneazo-β-naphthols. This, together with the fact that, with the diazosulphonates derived from such components as aniline, toluidine, 2 : 5-dichloroaniline, and anthranilic acid, no formation of phthalazine derivatives was observed, the presence of a nitro-group being, in fact, essential, suggests that the latter reaction is favoured by a powerful — *I* effect, whilst conversion into the benzeneazo-β-naphthol is facilitated by a + *T* effect. The observation that the new reaction does not occur with the derivative from diazotised sulphanilic acid may possibly be explained by the presence of the anion $\overset{++}{S}(\bar{O})_3$ in the alkaline medium, but the close polar similarity of the NO_2 and SO_2R groups suggests that an examination of the derivatives from diazotised sulphanilic esters or *p*-aminophenylsulphones would be of interest.

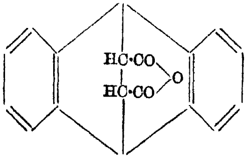
The scheme given on p. 123 summarises the main results (including those obtained on methylation of the phthalaz-1-ones, which cannot be dealt with in detail in this Report), the constitutions being those provisionally assigned by the authors. The structure (VI), however, is open to the criticism that a nitrogen atom with two unshared electron pairs could scarcely be stable in juxtaposition to an ammonium nitrogen atom. A more probable constitution for this substance is the dihydrophthalaz-1-one structure (XV). 3 : 4-Elimination of acetic acid from its betaine form (XVI) would then readily explain its conversion into the phthalaz-1-one (VIII). The formation from the diazosulphonate would be represented by the following scheme, which also suggests a reason for the facilitating effect of — *I* groups in the substituent R (see above).

[99] F. M. Rowe, E. Levin, and A. T. Peters, *J.*, 1931, 1067; *A.*, 835.
[1] F. M. Rowe, M. A. Himmat, and E. Levin, *J.*, 1928, 2556; *A.*, 1928, 1262.
[2] F. M. Rowe, C. Dunbar, and N. H. Williams, *J.*, 1931, 1073; *A.*, 835.



This view of the structure (XV) receives support from the fact that preliminary experiments have recently indicated that *N*-methyl derivatives of substances of this type can be prepared.[3]

Anthracene.—Certain evidence has been adduced in favour of the Armstrong rather than the Graebe–Liebermann structure for anthracene. Thus reduction of active benzyloxanthrone-2-carboxylic acids affords inactive 9-benzylanthracene-2-carboxylic acid,[4] whilst the presence of two double linkings at the 9- and 10-positions agrees well with the observation that anthracene reacts additively with αβ-unsaturated acids and esters to form stable derivatives of the type anthracene-9 : 10-*endo*maleic anhydride [5] (I). Such arguments are based, however, on a static conception, and it seems unlikely that the 9 : 10-bridged anthracene form would be any more permanent than is the Dewar phase in benzene.[6]



(I.)

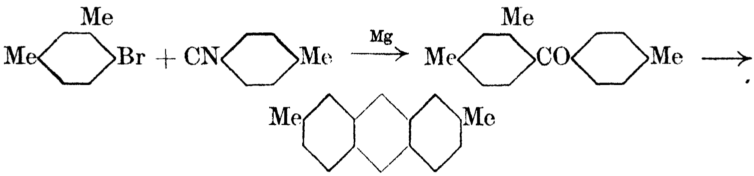
[3] Private communication from Professor F. M. Rowe.

[4] H. Goudet, *Helv. Chim. Acta*, 1931, **14**, 379; *A.*, 619.

[5] O. Diels and K. Alder, *Annalen*, 1931, **486**, 191; *A.*, 848.

[6] Compare E. Clar, *Ber.*, 1931, **64**, [*B*], 1676, 2193; *A.*, 1044, 1292.

Alkylanthracenes. The presence of 2 : 6- and 2 : 7-dimethyl-,* 2 : 3 : 6-trimethyl-, and 2 : 3 : 6 : 7-tetramethyl-anthracene in low-temperature tar has been confirmed by direct synthesis of these hydrocarbons.[7] The appropriate methyl-substituted benzophenone (prepared by condensation of the Grignard compound of a halogenomethylbenzene with *p*-toluonitrile) is slowly converted into the anthracene on heating :



Aromatic hydrocarbons may be conveniently alkylated by treatment with the appropriate alcohol and 80% sulphuric acid at 70—80°.[8] Thus, with benzyl alcohol, toluene and *o*-xylene afford, in addition to phenyl-*p*-tolylmethane and 4-benzyl-*o*-xylene, anthracene and 1-methylanthracene, respectively, the latter resulting from oxidation of the intermediate 9 : 10-dihydro-derivatives.

Owing to their carcinogenetic properties the synthesis of benz- and dibenz-anthracenes has recently assumed considerable importance. Distillation of 1-benzyl-2-methylnaphthalene with zinc dust affords mainly 1 : 2-benzanthracene together with a little of the 2 : 3-compound, whilst the corresponding ketone gives the 1 : 2-derivative exclusively.[9] By the condensation of 2-methylnaphthalene with β-naphthoyl chloride, E. Clar [10] obtained 2-methyl-1 : 2′-dinaphthyl ketone, pyrogenic decomposition of which gives 1 : 2 : 5 : 6-dibenzanthracene. In the similar decomposition of 2-methyl-1 : 1′-dinaphthyl ketone J. W. Cook [11] has shown that isomerisation to the 1 : 2′-ketone probably precedes cyclisation, since 1 : 2 : 5 : 6-dibenzanthracene is again formed and not the 1 : 2 : 7 : 8-compound (as stated by Clar). The same compound is obtained by pyrolysis of 1 : 4′-dimethyl-1 : 1′-dinaphthyl ketone with elimination of the methyl group in the α-position to a condensed ring.

* Described by J. Lavaux and M. Lombard (*Bull. Soc. chim.*, 1910, [iv], **7**, 539; *A.*, 1910, i, 548) as the 2 : 7-, and 1 : 6- or 1 : 7-derivatives, respectively.

[7] G. T. Morgan and E. A. Coulson, *J.*, 1929, 2203, 2551; 1931, 2323; *A.*, 1929, 1436; 1930, 80; 1931, 1282.

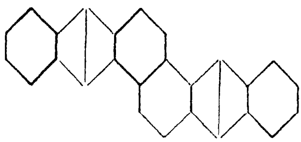
[8] H. Meyer and K. Bernhauer, *Monatsh.*, 1929, **53** and **54**, 721; *A.*, 1929, 1441.

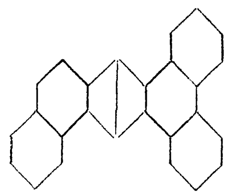
[9] K. Dziewoński and E. Ritt, *Bull. Acad. Polonaise*, 1927, **3**, [*A*], 181; *A.*, 1928, 52.

[10] *Ber.*, 1929, **62**, [*B*], 350; *A.*, 1929, 435.

[11] *J.*, 1931, 487, 489; *A.*, 612.

By the action of Grignard reagents on 1 : 2 : 5 : 6-dibenzanthraquinone and dehydration of the resulting diols a series of 9 : 10-dialkyl-1 : 2 : 5 : 6-dibenzanthracenes has been prepared:[12] the spectrum of the dibenzyl derivative is almost identical with that of the carcinogenetic mixture obtained by the action of aluminium chloride on tetralin.[13] Similar spectra are shown by phenanthranaphthene and phenanthrafluorene. Pyrogenic decomposition of 1 : 5-dibenzoyl-2 : 6-dimethylnaphthalene affords 2′ : 1′-anthraceno-1 : 2-anthracene[14] (II), and 1 : 2 : 3 : 4 : 5 : 6-tribenzanthracene (III) is obtained by similar methods.[15]

(II.) 

 (III.)

Anthraquinone derivatives. According to A. Meyer[16] conversion of anthraquinone-α-sulphonic acid into the β-acid by heating with sulphuric acid occurs only in the presence of metallic mercury. Since the β-acid is stable under the same conditions, the almost exclusive α-substitution observed[17] when anthraquinone is sulphonated in the presence of mercury salts cannot be due to the primary formation of the β-acid and subsequent isomerisation. Disulphonation of anthraquinone in the presence of mercury salts gives 1 : 5-(40—45%), 1 : 8-(23%), and traces of the 1 : 6- and 1 : 7-disulphonic acids. The α-directive catalytic influence of mercuric salts is also emphasised in a systematic re-investigation of the sulphonation of α-chloro- and dichloro-anthraquinones by A. A. Goldberg,[18] in the course of which 1 : 2 : 3-, 1 : 2 : 5-, 1 : 2 : 6-, 1 : 2 : 7-, 1 : 3 : 6-, 1 : 3 : 7-, 1 : 4 : 5-, and 1 : 4 : 6-trichloroanthraquinones are synthesised and oriented.

An interesting series of Δ^2-tetrahydroanthraquinones hydrogenated in the "twin" positions (designated as γ in naphthalene and δ in anthracene), obtained by addition of hydrocarbons with

[12] J. W. Cook, *loc. cit.*

[13] I. Hieger, *Biochem. J.*, 1930, **24**, 505; *A.*, 1930, 807.

[14] E. Clar, F. John, and B. Hawran, *Ber.*, 1929, **62**, [*B*], 940, 950; *A.*, 1929, 689.

[15] L. F. Fieser and E. M. Dietz, *ibid.*, p. 1827; *A.*, 1929, 1055.

[16] *Compt. rend.*, 1926, **183**, 519; *Bull. Soc. chim.*, 1927, [iv], **41**, 1627; *A.*, 1926, 1146; 1928, 781.

[17] H. E. Fierz-David, *Helv. Chim. Acta*, 1927, **10**, 197; 1928, **11**, 197; *A.*, 1927, 463; 1928, 293.

[18] *J.*, 1931, 1771; *A.*, 1062.

conjugated double linkings to benzo- and naphtha-quinones was mentioned in Part I of last year's Report.[19]

Molecular Compounds.

Under this heading some reference will also be made to the related subjects of association and chelation. If these phenomena are approached from the merely physical point of view, their explanation may be attempted exclusively in terms of dipole association and intermolecular forces due to the residual valency fields of the molecules or van der Waals forces. Many chemists, however, although admitting the importance of the considerations mentioned, prefer to regard the formation of new chemical molecules as a principal factor. Thus, N. V. Sidgwick[20] in particular has represented association as involving the formation of new molecules by means of co-ordinate linkages, and the extension of this view to molecular compounds in general would seem reasonable.[21] Molecular compound formation and association will then be regarded as similar intermolecular co-ordination phenomena between different and like molecules respectively, whilst chelation may be regarded as the analogous intramolecular process. It may be pointed out that this view follows the trend of modern chemical theory, which has been increasingly to attempt the representation by definite structural formulæ of complexes at first regarded as indefinite assemblages, the most important instance of this being Werner's theory, and another recent one the polymerisation theory of H. Staudinger.[22]

The isolation of a crystalline specimen is definite evidence of a chemical fact, but it is necessary to bear in mind that forces of the second order may contribute largely to the stability of a crystal assemblage. A true molecular compound will survive, to some extent at least, in the liquid or dissolved condition, and proof of this survival in the liquid state is very desirable. To take a recent example, compounds have been isolated in which either deoxycholic acid or *apo*cholic acid (dihydroxy-carboxylic acids, saturated and containing one double bond, respectively) is associated with 8 mols. of either stearic or palmitic acid or of cetyl alcohol.[23] It is difficult to believe that these are united by chemical bonds.

The recent appearance of a new edition of the important mono-

[19] *Ann. Reports*, 1930, **27**, 89.

[20] " The Electronic Theory of Valency," 1927, p. 132.

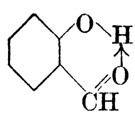
[21] T. M. Lowry, *Chem. and Ind.*, 1924, **43**, 218; G. M. Bennett and G. H. Willis, *J.*, 1929, 256; *A.*, 1929, 436.

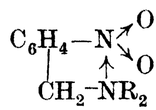
[22] *Ann. Reports*, 1929, **26**, 105—115.

[23] H. Rheinboldt, *Z. physiol. Chem.*, 1929, **180**, 180; *A.*, 1929, 443.

graph on molecular compounds by P. Pfeiffer [24] makes available an admirably classified survey of this field.

Chelate Compounds.—The chelate ring in *o*-substituted aromatic compounds, first suggested by P. Pfeiffer [25] for 1-hydroxyanthraquinone, was closely studied by N. V. Sidgwick and his colleagues.[26] An examination has now been made [27] of the parachors of certain aromatic compounds having the chelate ring. Four substances of the type *o*-$C_6H_4(OH)X$ (where X is NO_2, CHO, or CO_2Me), such as (I), consistently show a defect in their parachor values of 14·4 below that calculated (due allowance being made for the presence of a six-membered ring), whereas the corresponding methyl ethers give normal values. Of this defect, 1·6 is regarded by the authors as due to the transferred electron and 12·8 as associated with the rise in the covalency of hydrogen from 1 to 2. In passing from ter- to quinque-valent phosphorus in the chlorides there is a similar contraction of 25 units. These figures can equally well be numerically explained by means of formulæ involving singlet linkages.[28] S. Sugden regards the hydrogen atom with four shared electrons as inconsistent with Pauli's principle. N. V. Sidgwick [29] contends that this is not so, a second quantum group being permissible, but that the odd electron of the singlet linkage would on the other hand be definitely anomalous.

(I.) 

 (II.)

Marked differences of boiling point and solubility have been ascribed to self-co-ordination in the *o*-nitrobenzyldialkylamines (II),[30] but the melting points of *o*-nitrodialkylanilines [31] should not be taken as evidence of chelation, and the four-membered ring which would be formed is improbable on stereochemical grounds. It seems unjustifiable, moreover, to postulate chelate rings involving hydrogen attached to carbon.[32]

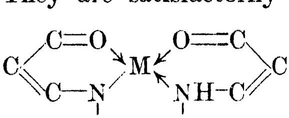
[24] "Organische Molekülverbindungen," 2nd Ed., 1927.
[25] *Annalen*, 1913, **398**, 137; *A.*, 1913, i, 879.
[26] *Ann. Reports*, 1924, **21**, 104.
[27] N. V. Sidgwick and N. S. Bayliss, *J.*, 1930, 2027; *A.*, 1240.
[28] S. Sugden, "The Parachor and Valency," 1930, p. 150; and *J.*, 1927, 1173; *A.*, 1927, 714.
[29] *Loc. cit.* and *J.*, 1924, **125**, 532; *A.*, 1924, i, 506.
[30] G. M. Bennett and G. H. Willis, *loc. cit.*
[31] H. H. Hodgson and A. Kershaw, *J.*, 1930, 497; *A.*, 1930, 595.
[32] W. Kistiakowski, *Z. physikal. Chem.*, 1928, **137**, 383; E. de B. Barnett and J. A. Low, *Ber.*, 1931, **64**, [*B*], 49; T. M. Lowry and W. V. Lloyd, *J.*, 1929, 1784; *A.*, 1929, 22, 1186; 1931, 341.

A number of chelate metallic compounds are referred to in the following section.

The subject of association cannot be discussed here in detail, but reference may be made to reviews of the evidence from observations of molecular polarisation by J. Errara [33] and C. P. Smyth.[34]

Metal Co-ordination Compounds.—The lithium halides form with aliphatic amines a series of compounds decomposing at or below laboratory temperature and containing 1—4 and sometimes 5 molecules of amine per atom of lithium.[35]

Compounds of the type MB,HB [where HB is ψ-indoxyl-*spiro*-*cyclo*pentane and M is lithium, sodium or potassium], soluble in toluene, are formed even in presence of a large excess of the alkali.[36] They are satisfactorily represented as co-ordination compounds, the metal being 4-covalent and combined as in the annexed formula. Alkali-metal derivatives of diketonic substances and of salicylaldehyde tend to form compounds with a second molecule of the parent substance; and alkali *o*-nitrophenoxides combine with one molecule of salicylaldehyde.[37] All these products are bichelate compounds with 4-covalent metal atoms.



A number of addition compounds of calcium, strontium, and barium halides with one, two, or three molecules of mono- and di-methylaminoacetic acid and betaine have been described,[38] such as $CaBr_2,X_3$; $BaI_2,X_2,4H_2O$; $SrCl_2,X,4H_2O$, where X is a molecule of the *N*-methylated glycine. Following Pfeiffer,[39] the authors formulate them with the carboxyl group co-ordinated to the metal, the alkylamino-groups being left free (I). The survival of a free amino-group is, however, improbable: the formula (II) is to be preferred, as it overcomes this difficulty and at the same time shows the analogy of the betaine complexes with the others.

$$\{[Me_2N{\cdot}CH_2{\cdot}C(OH){:}O]_2Ba(H_2O)_4\}I_2 \quad [(Me_2\overset{\oplus}{N}H{\cdot}CH_2{\cdot}C\overset{\ominus}{O_2})_2Ba(H_2O)_4]I_2$$

(I.) (II.)

[33] "The Dipole Moment and Chemical Structure," P. Debye, 1931, p. 101.

[34] "Dielectric Constant and Molecular Structure," 1931, p. 169; C. P. Smyth and others, *J. Amer. Chem. Soc.*, 1929, **51**, 1736, 3312; 1930, **52**, 1824; *A.*, 1929, 994; 1930, 135, 841. See also N. V. Sidgwick, *loc. cit.* and *Z. Elektrochem.*, 1928, **34**, 445; C. T. Zahn, *Physical Rev.*, 1931, [ii], **37**, 1516; *A.*, 1928, 13; 1931, 895.

[35] A. Simon and R. Glauner, *Z. anorg. Chem.*, 1929, **178**, 177; *A.*, 1929, 431.

[36] N. V. Sidgwick and S. G. P. Plant, *J.*, 1925, **127**, 209; *A.*, 1925, i, 298.

[37] N. V. Sidgwick and F. M. Brewer, *ibid.*, p. 2379; F. M. Brewer, *J.*, 1931, 361; *A.*, 1926, 71; 1931, 443.

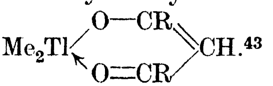
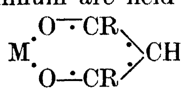
[38] W. K. Anslow and H. King, *Biochem. J.*, 1928, **22**, 1253; *A.*, 1928, 1362.

[39] *Op. cit.*, p. 140.

A series of compounds of calcium chloride with four and of calcium iodide with six molecules of various amides such as urea, thiourea, urethane, phenylurea, and antipyrine have been prepared.[40]

o-Phenylenediamine and *o*-tolylenediamine form a number of complexes with cadmium and zinc chlorides and bromides containing either two, three, or four molecules of amine per atom of the metal,[41] such as $\left[Zn\left(\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}>C_6H_4\right)_n\right]Br_2$, and there are indications of the occurrence of isomerism. The octammine type is unusual and therefore of particular interest: a cubic configuration is suggested. One or two complexes with *m*- and *p*-phenylenediamines are described, but evidence as to their molecular complexity would be desirable.

A study of the conductivities in acetone and of the parachors of some sulphonium and ammonium mercuri-iodides leads to the conclusion that they should be formulated as $[R_4N]^+[HgI_3]^-$ and $[R_3S]^+[HgI_3]^-$ and that the negative ion may be $I^-Hg<\begin{smallmatrix}I\\I\end{smallmatrix}$ or $I^-Hg\begin{smallmatrix}\cdot I\\ \cdot I\end{smallmatrix}$ The compound of mercuric iodide and dibenzyl sulphide is a non-electrolyte and may be written $R_2S—Hg<\begin{smallmatrix}I\\I\end{smallmatrix}$ or alternatively with singlet linkages.[42]

Remarkably stable chelate compounds of dimethylthallium with β-diketones and salicylaldehyde have been prepared, a typical structure being .[43] Parachor determinations on these and other derivatives of β-diketones with beryllium and aluminium are held by S. Sugden to point to the formula of the type  with singlet linkages.[44] It is here again equally possible to reconcile them with the alternative formula. The free diketones may contain some chelate form and some open-chain diketone.

The hydrocarbons stilbene, dimethylbutadiene, and carotene yield definite compounds with antimony and ferric chlorides of the composition $X,2MCl_3$.[45]

[40] F. R. Greenbaum, *J. Amer. Pharm. Assoc.*, 1929, **18**, 784; *A.*, 1929, 1169.

[41] W. Wahl, *Förh. III nord. Kemistmötet*, 1928, 172; *A.*, 1929, 157.

[42] H. J. Cavell and S. Sugden, *J.*, 1930, 2572; *A.*, 26.

[43] R. C. Menzies, N. V. Sidgwick, E. F. Cutcliffe, and J. M. C. Fox, *J.*, 1928, 1288; *A.*, 1928, 745.

[44] *J.*, 1929, 316; *A.*, 1929, 427; compare N. V. Sidgwick and L. E. Sutton, *J.*, 1930, 1472; *A.*, 1930, 1052.

[45] H. von Euler and H. Willstaedt, *Arkiv Kemi, Min. Geol.*, 1929, **10**, *B*, 9; A., 1930, 333.

A stable pink complex of nickel chloride with three molecules of αα′-dipyridyl has been resolved into optically active forms through the tartrate. The salt $[Ni,3dipy]Cl_2,6H_2O$ had $[\alpha]_{5461}$ + 550°, the activity vanishing rapidly in aqueous solution.[46]

Nickel cyanide combines with aliphatic and aromatic amines, the complexes containing one or two molecules of the base.[47] The lack of further co-ordinating power in the compound

$$[Ni(CN)_2,CH_2Ph{\cdot}CH_2{\cdot}NH_2]$$

is held to show that the nickel is 4-covalent, the phenyl nucleus providing one point of attachment.

The molybdenum derivatives of several β-diketones prove to have the composition $MoO_2[R{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}R]_2$ and are typical co-ordination compounds.[48]

The discovery of bivalent silver salts [49] has been followed by the preparation of several complexes of the type $[AgB_2]X_2$, where B is α-phenanthroline [50] or αα′-dipyridyl.[51]

In forming co-ordination compounds with copper salts, the molecule of thiourea (tu) tends to form a bridge between metal atoms so that, besides the simple compound $[Cu,2tu]NO_3,H_2O$, there result others such as $[Cu_2,5tu](NO_3)_2,2H_2O$; $[Cu_3,7tu](NO_3)_3$; $[Cu_5,11tu](NO_3)_5,8H_2O$. The cyclic ethylenethiourea (= etu) does not cause this complexity, and a series of compounds results such as [Cu,4etu]X, [Ag,4etu]X, $[Cd,4etu]X_2$, $[Hg,3etu]X_2$, $[Pd,4etu]X_2$ together with one or two complexes with lower co-ordination numbers such as [Ag,3etu]Cl.[51a]

The co-ordination of chloroplatinic and chloroplatinous acids with αβγ-triaminopropane, $CH_2(NH_2){\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2$, yields the interesting compounds

$$\left[\overset{\oplus}{N}H_3{\cdot}CH_2{\cdot}\overset{*}{C}H\begin{matrix}-NH_2\searrow \\ CH_2{\cdot}NH_2\nearrow\end{matrix}PtCl_4\right]Cl \text{ and } \left[\overset{\oplus}{N}H_3{\cdot}CH_2{\cdot}\overset{*}{C}H\begin{matrix}-NH_2\searrow \\ CH_2{\cdot}NH_2\nearrow\end{matrix}PtCl_2\right]Cl,$$

which were each resolved into their optically active components by F. G. Mann.[52] The central carbon atoms (*) are asymmetric. A complex with the same base of the formula $[PtB_2]I_2$ was also prepared in which all the amino-groups are definitely engaged, making the metal 6-covalent. A number of other co-ordination compounds

[46] G. T. Morgan and F. H. Burstall, *J.*, 1931, 2213; *A.*, 1168.

[47] E. Hertel, *Z. anorg. Chem.*, 1929, **178**, 202; *A.*, 1929, 380.

[48] G. T. Morgan and R. A. S. Castell, *J.*, 1928, 3252.

[49] *Ann. Reports*, 1928, **25**, 44.

[50] W. Hieber and F. Mühlbauer, *Ber.*, 1928, **61**, 2149; *A.*, 1381.

[51] G. T. Morgan and F. H. Burstall, *J.*, 1930, 2594; *A.*, 234.

[51a] *Idem*, *J.*, 1928, 143; *A.*, 1928, 278.

[52] *J.*, 1927, 1224, 2904; 1928, 890, 1261; 1929, 409, 651; *A.*, 1927, 754; 1928, 157, 622, 745; 1929, 545, 678. Compare *Ann. Reports*, 1926, **23**, 109.

of nickel, cobalt, and platinum with various aliphatic diamines such as mono- and tri-aminotriethylamine, β-methyl-, β-hydroxy-, and β-bromo-trimethylamine have been described by the same author.

The volatile acetylacetonate of trimethylplatinum [53] and a similar derivative of diethylgold are evidently chelate compounds. The latter was isolated in the course of experiments with diethylgold bromide [54] in which a number of other compounds of 4-covalent gold were described such as the amines $[Et_2AuBr,NH_3]$, $[Et_2AuBr,Py]$, $[Et_2Au\ en]Br$, and $[Pr^{\alpha}{}_2Au\ en]Br$. From gold bromide there were also prepared deep-coloured complexes $[AuBr_3,B]$ (where B is pyridine, quinoline, *iso*quinoline, 2-aminopyridine, or di-2-pyridylamine) and the compounds $[AuBr_2,Py_2]Br$ and $[Au\ en_2]Br_3$.

Compounds with Co-ordinated Oxygen.—Aliphatic alcohols yield crystalline hexacyanocobaltiates of the types $[R\overset{\oplus}{O}H_2]_3[Co(CN)_6]$ and $[R\overset{\oplus}{O}H_2]_2H[Co(CN)_6]$ which are evidently normal alkoxonium derivatives.[55] More complicated compounds are formed from alcohols, ethers, and acetone with hydrogen chloride or bromide at low temperatures,[56] such as $Et_2O,2HX$ and $Et_2O,5HCl$. Triphenylcarbinol yields with sulphuric acid the compound $CPh_3{\cdot}OH,4H_2SO_4$.[57]

The coloration shown by cholesterol in chloroform with sulphuric acid is due to a red equimolecular compound, cholesterol sulphate.[58]

The shape of the solubility curves of a number of aliphatic and cyclic ethers,[59] of the isomeric butyl alcohols,[60] and of *cyclo*hexanol in water [61] indicates that there is some combination between these substances and the water. There are several factors involved, but the figures for the isomeric methyl butyl ethers show the expected increase of solubility arising from the increased co-ordinating power of an oxygen atom under the influence of the polar effects of the adjacent methyl groups. That dibenzyl ether causes the partial dissociation of benzoic and acetic acids dissolved in it may also be attributed to co-ordination of the acids with the ether.[62]

[53] R. C. Menzies, *J.*, 1928, 565; *A.*, 1928, 509.

[54] C. S. Gibson and J. L. Simonsen, *J.*, 1930, 2531; C. S. Gibson and W. M. Colles, *J.*, 1931, 2407; *A.*, 78, 1316.

[55] F. Hölzl, T. Meier-Mohar, and F. Viditz, *Monatsh.*, 1929, **52**, 73; *A.*, 1929, 898.

[56] D. McIntosh, *Proc. Nova Scotian Inst. Sci.*, 1928, **17**, 112, 116; *A.*, 1929, 292.

[57] H. R. Dittmar, *J. Physical Chem.*, 1929, **33**, 533; *A.*, 1929, 656.

[58] V. J. Nikolaev and S. A. Krastelevskaja, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 1211; *A.*, 1929, 61.

[59] G. M. Bennett and W. G. Philip, *J.*, 1928, 1930; *A.*, 1928, 944.

[60] D. C. Jones, *J.*, 1929, 799; *A.*, 1929, 638.

[61] N. V. Sidgwick and L. E. Sutton, *J.*, 1930, 1323; *A.*, 1930, 988.

[62] G. M. Bennett and G. H. Willis, *J.*, 1928, 2305; *A.*, 1928, 1089.

A qualitative test for weak bases, depending upon the formation of ferrichlorides in solution, is given by most oxygen, nitrogen, and sulphur compounds.[63]

A crystalline sulphate of nitrobenzene, $[Ph{\cdot}NO_2H]HSO_4$, has been described, which is an electrolyte.[64] The increase in the conductivity of sulphuric acid caused by addition of *p*-nitrotoluene is greater than with nitrobenzene, whilst dinitrobenzene has no such effect. Nitrobenzene forms an equimolecular compound with stannic chloride and the existence of the compounds $2PhNO_2,SnCl_4(Br_4)$ is deduced from the viscosity curves of mixtures of these substances.[65]

A study of the freezing points of mixtures of carbon tetrachloride and chloroform with acetone and ether[66] shows the existence at low temperatures of a number of compounds such as CCl_4,Et_2O; $CCl_4,2Et_2O$; $CCl_4,COMe_2$; $CHCl_3,3Et_2O$; $CHCl_3,2Et_2O$; $CHCl_3,Et_2O$; and $2CHCl_3,Et_2O$.

Compounds of Polynitro-aromatic Substances.—The largest group of molecular compounds (apart from co-ordination compounds of the metals) comprises those formed by the union of substances such as di- and tri-nitrobenzene or picric acid with bases, aromatic hydrocarbons or their derivatives. In the development of our knowledge of this class of complex J. J. Sudborough,[67] A. Werner,[68] and P. Pfeiffer[69] took prominent parts.

The problem of their structure is a difficult one : but it is clear from a general review of the facts that, if they are formed by mutual co-ordination of the components, the hydrocarbon or base is the donor molecule and the nitro-compound the acceptor.[70] Their depth of colour is in general roughly parallel with their stability[71] and the influence of polar groups substituted in either component is consistent with this view.

A further illustration of this point is provided by the series of compounds described by C. A. Buehler and his colleagues from *m*-dinitrobenzene, 2 : 4-dinitrotoluene, 2 : 4-dinitrophenol, and chloro- and bromo-2 : 4-dinitrobenzenes with a series of bases,

[63] R. Robinson, *J.*, 1925, **127**, 768; *A.*, 1925, ii, 606.

[64] E. Cherbuliez, *Helv. Chim. Acta*, 1923, **6**, 281; *A.*, 1923, i, 452. Compare I. Masson, *J.*, 1931, 3200.

[65] F. de Carli, *Atti R. Accad. Lincei*, 1929, [vi], **10**, 186, 250, 372; *A.*, 1930, 26, 284.

[66] W. F. Wyatt, *Trans. Faraday Soc.*, 1929, **25**, 43; *A.*, 1929, 254.

[67] *J.*, 1901, **79**, 522; 1910, **97**, 773; 1916, **109**, 1339.

[68] *Ber.*, 1909, **42**, 4324; *A.*, 1910, i, 20.

[69] *Op. cit.*

[70] G. M. Bennett and G. H. Willis, *loc. cit.*

[71] P. Pfeiffer, *op. cit.*, p. 348.

hydrocarbons and naphthols.[72] The stability of the products diminishes with substitution in the dinitro-compound in the order Cl>Br>OH>H>Me>NH_2. *p*-Chloronitrobenzene also combines with α-naphthol.

Other recent additions to the list of such compounds are several from tetryl with aromatic hydrocarbons,[73] a compound of 1 : 3 : 4 : 5-tetranitrobenzene with benzene (1 : 1),[74] and of 4 : 4′-dithiolarseno-benzene with picric acid (1 : 2).[75] Others are mentioned in the discussion below.

The stability of such complexes in solution has been the subject of repeated investigation. R. Behrend in 1894,[76] by measuring the joint solubilities of anthracene and picric acid in alcohol at 25°, found a dissociation constant for the compound of 4·7—5·7; and the union of picric acid and β-naphthol was studied in a similar manner.[77] Determinations of freezing points of solutions of the components in nitrobenzene by F. S. Brown [78] show a dissociation constant for naphthalene picrate of 0·23 and for naphthalene–*s*-trinitrobenzene of 0·46. The free energy of formation of the former compound was calculated to be 2080 cals. per mol., which agrees well with the value 2150 cals. found by J. N. Brönsted from determinations of *E.M.F.* in the system naphthalene–picric acid–potassium chloride–hydrochloric acid–water.[79]

The same question has been examined by H. von Halban and E. Zimpelmann [80] by the photoelectric determination of the absorption of light in solutions of various concentrations at more than one temperature. The following values of the heats of formation (Q) and the equilibrium constants (K) at 25° were found :

Compound.	Solvent.	Q (cals.).	K.
Acenaphthene–*s*-trinitrobenzene ...	Tetrachloroethane	2450	0·41
Acenaphthene–*m*-dinitrobenzene ...	,,	1350	3·15
Acenaphthene–picric acid	,,	950	0·50
Anthracene–picric acid	Chloroform	3990	0·22

[72] C. A. Buehler with A. G. Heap, *J. Amer. Chem. Soc.*, 1926, **48**, 3168; with A. Hisey and J. H. Wood, *ibid.*, 1930, **52**, 1939; with C. R. Alexander and G. Stratton, *ibid.*, 1931, **53**, 4094; *A.*, 1927, 141; 1930, 905.

[73] N. N. Efremov and A. M. Tichomirova, *Ann. Inst. Anal. Phys. Chem.*, 1928, **4**, 65, 92.

[74] A. F. Holleman, *Rec. trav. chim.*, 1930, **49**, 112, 501; *A.*, 1930, 333, 900.

[75] S. Krishna and R. Krishna, *J. Indian Chem. Soc.*, 1929, **6**, 665; *A.*, 1929, 1320.

[76] *Z. physikal. Chem.*, 1894, **15**, 183; *A.*, 1895, ii, 71.

[77] B. B. Kuriloff, *ibid.*, 1897, **23**, 90, 673; *A.*, 1897, ii, 397, 484.

[78] *J.*, 1925, **127**, 345; *A.*, 1925, ii, 296.

[79] *Z. physikal. Chem.*, 1911, **78**, 284; *A.*, 1912, ii, 20.

[80] *Ibid.*, 1925, **117**, 461; *A.*, 1926, 25.

A precise investigation of such equilibria by the partition method has recently been published by T. S. Moore, F. Shepherd, and E. Goodall,[81] who have examined a range of substances wide enough to reveal the effects of substitution. Compound formation between picric acid and a series of aromatic substances in chloroform at 18° is calculated from indirect determinations of the free picric acid present. The latter is found by observing the concentration in an aqueous phase in contact with the chloroform. Similarly with aniline and a series of aromatic substances in chloroform at 25°, the aniline in the water phase being determined bromometrically. The assumption of (1 : 1)-combination gives good equilibrium constants *K*. A relatively small effect which the added substances exert on the partition curves is studied and is expressed by the "depression constants" below.

Picric Acid Compounds.

	K.		*K.*		*K.*
Benzene ...	0·09	Bromobenzene	0·09	Nitrobenzene	0·56
Toluene ...	0·12	*o*-Dichlorobenzene	0·10	*m*-Dinitrobenzene	1·03
o-Xylene ...	0·16	*p*- ,,	0·03	*o*-Nitrotoluene	0·41
m- ,, ...	0·14	*a*-Bromonaphthalene	0·23	*p*- ,, ...	0·57
p- ,, ...	0·16	Naphthalene	2·17	2 : 4-Dinitrotoluene	0·67
Mesitylene	0·18	*a*-Methylnaphthalene	2·76	*s*-Trinitrotoluene ...	1·02
Tetrahydronaphthalene	0·26	*β*- ,,	3·44	Nitronaphthalene ...	1·02

Aniline Compounds.

	K.		*K.*
Nitrobenzene	0·01	*m*-Dinitrobenzene	0·17
a-Nitronaphthalene	0·02	*p*- ,, ...	0·18
p-Chloronitrobenzene	0·03	2 : 4-Dinitrotoluene	0·15
m-Bromonitrobenzene	0·06	1 : 5-Dinitronaphthalene	0·57
		s-Trinitrotoluene	0·56

Depression Constants.

Picric acid.		*Aniline.*			
Hexane ...	0·54	*o*-Nitrotoluene	0·01	*a*-Bromonaphthalene	0·06
*cyclo*Hexane	0·48	*p*- ,, ...	0·02	Carbon tetrachloride	0·10
Hexachlorobenzene	0·38	Toluene	0·12	Naphthalene	0·07
Carbon tetrachloride	0·27	*p*-Xylene..............	0·15	*o*-Dichlorobenzene	0·06
		a-Methylnaphthalene	0·09	*p*-Dichlorobenzene	0·06
		β- ,,	0·09	Bromobenzene	0·05

The depression constants may be regarded as minor influences on mutual solubility arising from differences of polarity among the substances, and the smaller values of *K* in the aniline series may be attributed to increases of solubility arising in a similar way, although some would regard the colour produced as evidence of combination. With di- and tri-nitro-compounds the authors regard the *K* values as representing combination of the aniline.

[81] *J.*, 1931, 1447; *A.*, 949.

In the picrate series the naphthalenes combine more than the benzenes and the union is increased by methyl groups but diminished by chlorine atoms in agreement with the general conclusion (p. 134) as to the function of the components.

There is, however, a large increase of combination evident when one or more nitro-groups are introduced into the molecule, although the converse result might have been expected from the opposite polar nature of the methyl and the nitro-group. The solutions in these cases, nevertheless, show relatively little colour. A pale yellow compound of picric acid with nitronaphthalene was isolated (previously detected from the freezing-point curve).[82]

The authors ascribe the different type of union here involved to mutual dipole association of nitro-groups in the two substances.[83] It is equally possible to attribute the union to the basic property of the nitro-group as exhibited in nitrobenzene sulphate (p. 134).

The stability and conditions for isolation of solid molecular compounds have been discussed by O. Dimroth [84] and E. Bamberger. For the reaction $A + B \rightleftharpoons C$, they write the equilibrium constant $K = [C]/[A][B] = G.c/ab$, in which a, b, and c are the solubilities of A, B, and C in a given solvent, and G is a stability constant for the crystalline molecular compound C which is independent of the solvent used. G may also be written as $S_C/S_A.S_B$, where S_C, S_A, and S_B are the degrees of saturation of the compounds C, A, and B respectively. This law is verified for anthracene picrate with the solvents alcohol, chloroform, ether, petroleum, and carbon tetrachloride. It leads to a precise statement of the conditions under which a solvent causes the decomposition of a molecular compound. No decomposition occurs when the quotient (solubility of the more soluble component)/(solubility of the less soluble component) $< G$.

By determining the free picric acid in a small volume of water in equilibrium with partly decomposed compounds, the following relative order of increasing stabilities is found for a series of picrates: benzene < fluorene < anthracene < indene < phenanthrene < naphthalene < acenaphthene < α-methylnaphthalene < β-methylnaphthalene.

The problem of formulating these substances has attracted considerable attention. Werner [85] argued that the nitro-group is

[82] P. L. Jovinet, *Mém. Poudres*, 1928, **23**, 36; *A.*, 1928, 1085.

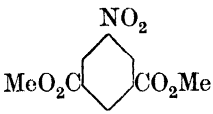
[83] The freezing-point curve of nitrobenzene with *m*-dinitrobenzene has meanwhile revealed the existence of an unstable (1 : 1) compound, and that of nitrobenzene and *s*-trinitrobenzene a (2 : 1) compound (D. L. Hammick, L. W. Andrew, and J. Hampson, *J.*, 1932, 171).

[84] *Annalen*, 1924, **438**, 67; *A.*, 1925, ii, 36.

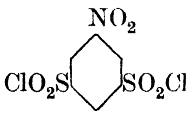
[85] *Loc. cit.* The argument from colour development would indicate combination of tetranitromethane with a wide range of unsaturated or basic substances; see E. M. Harper and A. K. Macbeth, *J.*, 1915, **107**, 87, 1824.

a point of attachment, since aliphatic nitro-compounds such as tetranitromethane and hexanitroethane yield similar complexes. Definite structural formulæ for the base–nitro-compound complexes were discussed by Sudborough in his earlier papers, but in 1915 [86] he adopted the residual valency conception of P. Pfeiffer, which may be represented by the typical formulæ $C_6H_3(NO_2)_3 \ldots C_{10}H_8$ and $C_6H_3(NO_2)_3 \ldots . C_{10}H_7{\cdot}NH_2$. This was also supported by J. Kenner.[87]

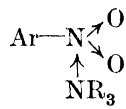
The idea that a more precise formulation should be possible has been recently revived [88] and it is suggested that the union must be through a single nitro-group, any others present in the same molecule having an indirect reinforcing effect. In support of this it was shown that, although molecular compounds of mononitrobenzenes (excepting nitrophenols) have hitherto been practically unknown, the substances (I) and (II), in which the nitro-group is similarly reinforced by other electron-attracting groups, do yield such complexes.



(I.)



(II.)



(III.)

The nitro-compound is regarded as united to an amine through the basic nitrogen atom as suggested by Werner and the union is now formulated as in (III). Combination with hydrocarbons is regarded as occurring with one ethylene bond in the polarised form $-\overset{\ominus}{C}H-\overset{\oplus}{C}H-$. The occurrence of 1 mol. of ethylene or of benzene in metal co-ordination compounds such as $[PtCl_2,NH_3,C_2H_4]$, $[Ni(CN)_2,NH_3,C_6H_6]$, and the nickel cyanide complex mentioned on p. 132, points definitely to the provision of one covalency by one molecule of ethylene or one benzene nucleus.

The behaviour of dinitrobenzenes with ammonia should have some bearing on the question of structure here involved. W. E. Garner and his colleagues have found [89] that *m*-dinitrobenzene combines slowly with (anhydrous) ammonia, the complex then rapidly ionising to give a coloured negative ion containing the organic substance. The nature of the positive ion is less clear, but it is regarded as $\overset{\oplus}{NH_3}$ or $\overset{\oplus\oplus}{N_2H_6}$.

[86] *Loc. cit.*

[87] J. Kenner and M. Parkin, *J.*, 1920, **117**, 855.

[88] G. M. Bennett and G. H. Willis, *loc. cit.*

[89] M. J. Field, W. E. Garner, and C. C. Smith, *J.*, 1925, **127**, 1227; W. E. Garner and H. F. Gillbe, *J.*, 1928, 2889; *A.*, 1925, ii, 792; 1929, 29.

The question of the structure in the crystals of these molecular compounds has been attacked by the X-ray method [90] and it has been shown that they have crystal lattices distinct from those of their components. Suggestions are made as to the arrangement of the units, but the positions of the atoms have not been determined.

The formation of distinct yellow and red isomeric compounds of picric acid or dinitrophenols with halogenated amines is termed by E. Hertel " complex isomerism " and the substances are formulated as $[(NO_2)_3C_6H_2{\cdot}\overset{\ominus}{O}][\overset{\oplus}{N}H_3Ar]$ (yellow) and $HO{\cdot}C_6H_2(NO_2)_3 \ldots\ldots ArNH_2$ (red).[91]

The production of colour in the formation of molecular compounds is a circumstance which has been of considerable importance in their study. Mention may be made of some observations on halochromism in chalkone derivatives [92] and in styrylquinoxalines [93] and of a recent theory of the probable origin of colour in quinhydrones.[94]

The Bile Acids.

(Continued from *Ann. Reports*, 1928, **25**, 163.)

Important modifications in the formulæ of all the cholane derivatives must follow from the recent developments in this field. The new evidence indicates that ring III and probably also ring I are each seven- instead of six-membered (compare cholanic acid formula, p. 140).

The structure (III) originally assigned [95] to the tetrabasic acid $C_{16}H_{24}O_8$ obtained from pyrodeoxybilianic acid (I) through the dibasic diketo-acid $C_{23}H_{34}O_6$ (II) has been found to require revision.[96] The passage from the diketo-acid (II) to (III) involved the shortening of the side chain by two carbon atoms, and as related compounds such as choloidanic acid [97] retained their complete side chain under similar conditions, it seemed doubtful whether (II) was actually attacked in this way. The dibasic keto-acid, $C_{15}H_{22}O_5$ (IV), obtained by heating the tetrabasic acid (III), was reduced by

[90] E. Hertel, *Z. physikal. Chem.*, 1930, [*B*], **7**, 188; 1930, [*B*], **11**, 59, 77; *A.*, 1930, 668; 1931, 153.

[91] E. Hertel and K. Schneider, *ibid.*, 1930, **151**, 413; 1931, [*B*], **13**, 387; *A.*, 210, 1114.

[92] W. Dilthey, L. Neuhaus, and W. Schommer, *J. pr. Chem.*, 1929, [ii], **123**, 235; 1930, [ii], **124**, 81; *A.*, 1929, 1300; 1930, 604.

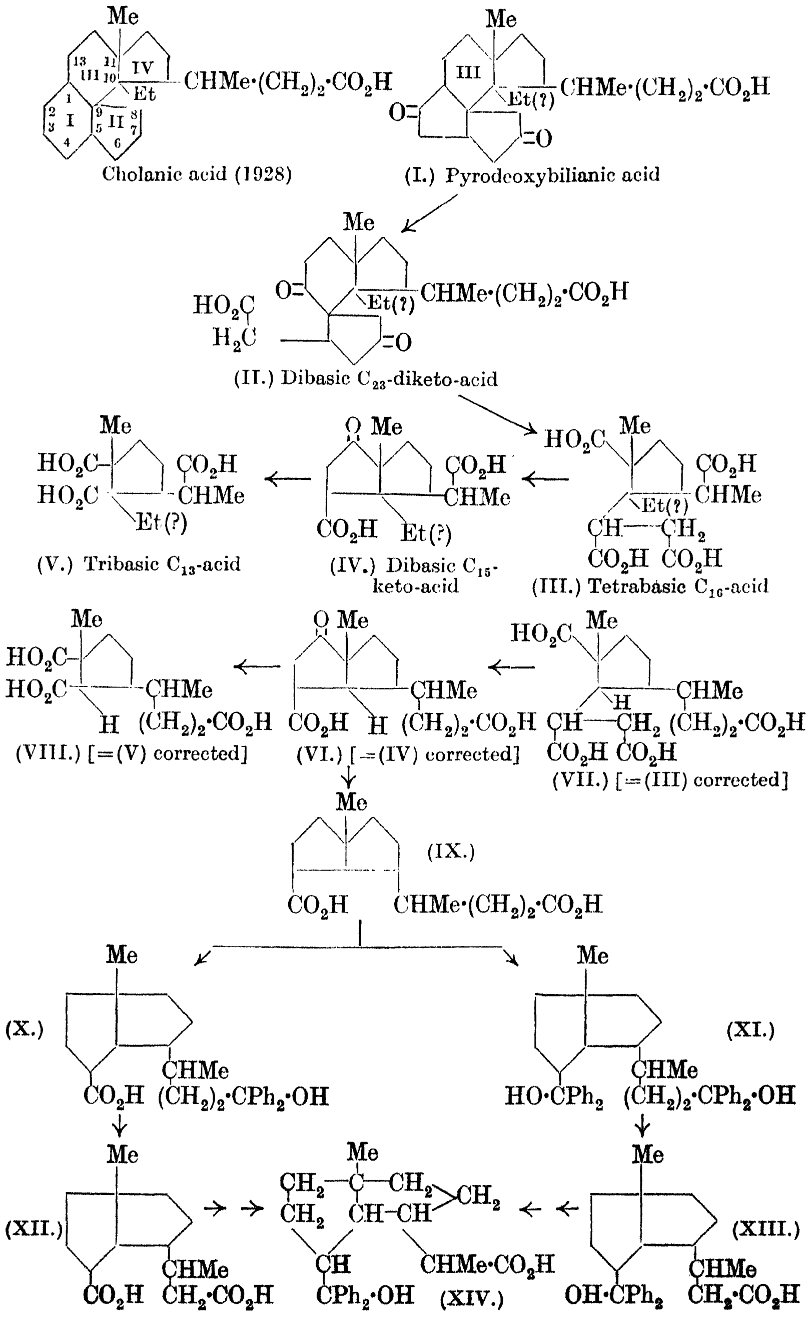
[93] G. M. Bennett and G. H. Willis, *loc. cit.*

[94] E. Weitz, *Z. Elektrochem.*, 1928, **34**, 538; *A.*, 1929, 190.

[95] H. Wieland and F. Vocke, *Z. physiol. Chem.*, 1928, **177**, 68; *A.*, 1928, 1007. Compare *Ann. Reports*, 1928, **25**, 160.

[96] *Idem, ibid.*, 1930, **191**, 69; *A.*, 1930, 1435.

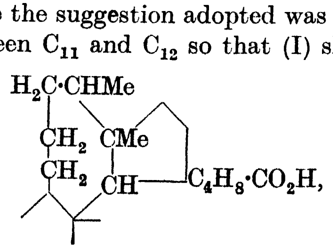
[97] *Ann. Reports*, 1927, **24**, 137.


Cholanic acid (1928)
(I.) Pyrodeoxybilianic acid
(II.) Dibasic C_{23}-diketo-acid
(V.) Tribasic C_{13}-acid
(IV.) Dibasic C_{15}-keto-acid
(III.) Tetrabasic C_{16}-acid
(VIII.) [=(V) corrected]
(VI.) [=(IV) corrected]
(VII.) [=(III) corrected]
(IX.)
(X.)
(XI.)
(XII.)
(XIV.)
(XIII.)

Clemmensen's method to the dibasic acid $C_{15}H_{24}O_4$ (IX), and the latter converted by the action of phenylmagnesium bromide on its ester into an acid tertiary alcohol (X) and a ditertiary alcohol (XI). The acid carbinol was oxidised to the dibasic acid $C_{14}H_{22}O_4$ (XII), whilst the ditertiary alcohol yielded the diphenylcarbinol derivative (XIII) of this acid. In either case a repetition of the Grignard and oxidation processes led finally to the carbinol acid (XIV) (derived from an acid $C_{13}H_{20}O_4$). This shortening of the side chain by one carbon atom at a time would be impossible if the dibasic keto-acid had structure (IV), but the alternative structure (VI) with side chain longer by $2CH_2$ groups is in complete agreement with these results. If structure (VI) be accepted for the acid $C_{15}H_{22}O_5$, the tetrabasic C_{16} acid must be (VII), not (III), and the tribasic acid $C_{13}H_{20}O_6$ must be (VIII) instead of (V). The occurrence of *n*-butane-$\alpha\gamma\gamma$-tricarboxylic acid together with (VII) in the oxidation products from the dibasic diketo-acid (II) is equally well accounted for by the new formulæ, which explain more readily the simultaneous production of α-methylglutaric acid.

Since the acids (VI), (VII), and (VIII) have two more carbon atoms in the side chain than was originally supposed, there must be a hydrogen atom and not an ethyl group in position 10 in these compounds. This, however, leaves C_2H_4 unaccounted for in the formulæ of the dibasic diketo-acid $C_{23}H_{34}O_6$ and all related substances. Two possibilities are discussed by the authors to meet this difficulty. The less probable assumption is that in the course of the oxidation of (II) a 10-ethyl group migrates to some other part of the molecule and is then oxidised away. The alternative conclusion seems almost inevitable, namely, that the missing atoms form part of ring III of the cholane skeleton. It has not been rigidly proved that this ring is six-membered: the available evidence is consistent with its being one of 7 carbon atoms.

In the first place the suggestion adopted was that a CHMe group was inserted between C_{11} and C_{12} so that (I) should be



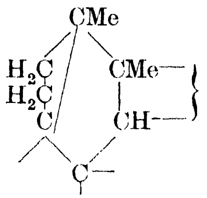
but later work has pointed to the CHMe group being between C_1 and C_9, whereby rings I and III will both be seven-membered.

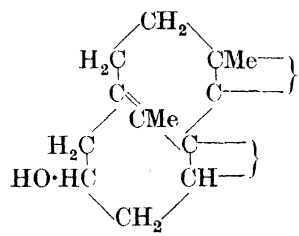
The first indication of this comes from a detailed study [98] of the

[98] H. Wieland and V. Deulofeu, *Z. physiol. Chem.*, 1931, **198**, 127; *A.*, 841.

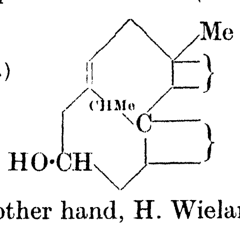
two dihydroxycholenic acids, $C_{24}H_{38}O_4$, obtained by dehydration of cholic acid.[99] Of these, one is catalytically reduced to deoxycholic acid, and consequently has the normal bile acid skeleton. The second (*apo*cholic acid) is not so hydrogenated and a more complicated relationship seemed possible. However, the two acids by the action of bromine yield with loss of hydrogen bromide the same dihydroxycholadienic acid, $C_{24}H_{36}O_4$. Catalytic reduction saturates only one of the two double bonds in this substance and the product is very similar to *apo*cholic acid but differs from it in rotatory power.

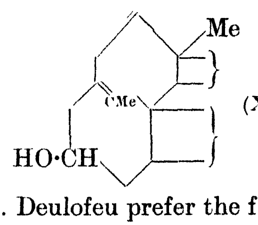
These results are in any case inconsistent with the earlier cholic acid formula with a six-membered ring III. For *apo*cholic acid cannot have its double bond between C_{12} and C_{13}, as it would then be readily reducible just as is the same bond in the cholatrienic acid from cholic acid. Nor has the other dihydroxycholenic acid an ethylenic linkage at C_{12}—C_{13}, since it does not yield the cholatrienic acid by loss of water. That a double bond may have wandered is probable, sulphuric acid and zinc chloride being the reagents used in the reaction, but it is unlikely that it will have migrated into another ring and consequently there must be seven members in ring III. W. Borsche and A. R. Todd [1] suggest that the inert

(XV.) 

 (XVI.)

double bond in these acids is in fact a bridge, and they represent ring III in *apo*cholic acid as (XV) with the CMe between C_{11} and C_{12}.

(XVII.) 

 (XVIII.)

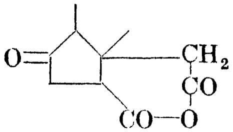
On the other hand, H. Wieland and V. Deulofeu prefer the formulæ (XVI), (XVII), and (XVIII) for *apo*cholic acid, dihydroxycholenic acid, and dihydroxycholadienic acid respectively. The environment of the central double bond explains its inertness.

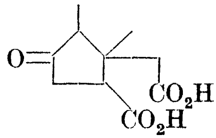
[99] F. Boedecker and H. Volk, *Ber.*, 1920, **53**, 1852; 1921, **54**, 2489; 1922, **55**, 2302; *A.*, 1921, i, 865; 1922, i, 1027.

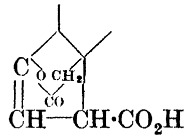
[1] *Z. physiol. Chem.*, 1931, **197**, 173; *A.*, 841.

*apo*Cholic acid yields by loss of water on heating a cholatrienic acid in which, again, one double bond resists hydrogenation. A little cholanic acid was, however, detected which suffices to confirm the normal carbon skeleton of these substances.

A closer examination of pyrocholoidanic acid has, moreover,[2] provided evidence that ring I is seven-membered. It is not a keto-anhydride acid as hitherto assumed (XIX) but a keto-lactonic acid.

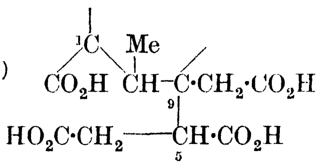

(XIX.)

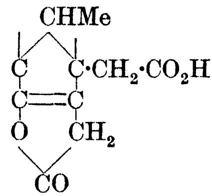

(XX.)


(XXI.)

Titration with cold alkali reveals a second carboxyl group (besides that in the side chain), and hot alkali three: diazomethane, moreover, yields a dimethyl ester. The dehydration thus involves only one carboxyl group and if the keto-acid (XX) is first formed, the keto-lactone structure (XXI) seems probable. But this formula is contrary to Bredt's rule that a double bond is not stable adjacent to the bridge head of a bridged six-membered ring.[3]

This difficulty is overcome by the use of the new formula so that choloidanic acid is (XXII) and the pyro-acid is (XXIII).

(XXII.)



(XXIII.)

The formation of two stereoisomerides is also accounted for.

These corrections are fundamental and further evidence will soon, it may be hoped, allow of a permanent revision of all the formulæ in the cholane group.

Ergosterol.

(Continued from *Ann. Reports*, 1927, **24**, 148.)

Chemical investigation of the phytosterols has been principally concerned with ergosterol[4] on account of the connection between

[2] H. Wieland, L. Ertel, and W. Schönberger, *Z. physiol. Chem.*, 1931, **197**, 31; *A.*, 841.

[3] J. Bredt, H. Thouet, and J. Schmitz, *Annalen*, 1924, **437**, 1; A. Windaus and A. Bohne, *ibid.*, 1925, **442**, 7; *A.*, 1924, i, 643; 1925, i, 552.

[4] Other sterols: see *Ann. Reports*, 1929, **26**, 211, and H. Wieland, with M. Asano, *Annalen*, 1929, **473**, 300; with G. A. C. Gough, *ibid.*, 1930, **482**, 36; with W. M. Stanley, *ibid.*, 1931, **489**, 31; F. Reindel and A. Weichmann, *ibid.*, 1930, **482**, 120; H. Sandqvist and J. Gorton, *Ber.*, 1930, **63**, [*B*], 1935; *A.*, 1929, 1200; 1930, 1431; 1931, 1154; 1930, 1578, 1431.

this compound and vitamin-*D*, the latter having been isolated as a crystalline isomeride of the sterol.[5]

Ergosterol, obtained from yeast, is purified as the acetate or the benzoate.[6] Its molecule, $C_{27}H_{42}O$, contains four rings, a hydroxyl group, and three double bonds. Complete reduction yields[7] ergostane, $C_{27}H_{48}$, a hydrocarbon isomeric but not identical with the similar products from cholesterol, coprosterol, and sitosterol. The carbon framework is shown to be similar to that of cholesterol by the observation of O. Diels and A. Karstens[8] that the main products of dehydrogenation of ergosterol with selenium are the same two crystalline hydrocarbons, $C_{18}H_{16}$ and $C_{25}H_{24}$, previously found as dehydrogenation products of cholesteryl chloride. It is therefore probable that ergostane is a stereoisomeride of cholestane. There are, indeed, indications that cholesterol may be converted into ergosterol by heat[9] and the saturated derivative of sitosterol is equally closely related.[10]

Oxidative degradation of ergosterol has yielded few results owing to the extreme sensitiveness of the sterol to all reagents : it absorbs oxygen (5 atomic proportions) from the air.[6] F. Reindel and K. Niederlander[11] have, however, isolated a tribasic acid, $C_5H_3(CO_2H)_3$, from the products of oxidation with nitric acid. This appears to be a *cyclo*pentadiene derivative arising from a 5-membered ring in the nucleus. An aldehyde, $C_5H_{11}{\cdot}CHO$, was also obtained by ozonisation, which yields on oxidation a methylglutaric acid, and points to the group $>C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe_2$ in the side chain of ergosterol.

When the sterol is catalytically reduced, two molecular proportions of hydrogen are added to give ergostenol, $C_{27}H_{46}O$, or three with formation of the completely saturated ergostanol, $C_{27}H_{48}O$.[12, 13, 14]

[5] Compare Biochemistry section of this report, p. 212.

[6] R. K. Callow, *Biochem J.*, 1931, **25**, 79; *A.*, 618.

[7] A. Windaus and W. Grosskopf, *Z. physiol. Chem.*, 1922, **124**, 8; *A.*, 1923, i, 75; F. Reindel and E. Walter, *Annalen*, 1928, **460**, 212; *A.*, 1928, 295.

[8] *Annalen*, 1930, **478**, 129; *A.*, 1930, 470. Compare O. Diels, W. Gädke, and P. Körding, *ibid.*, 1927, **459**, 1; *A.*, 1928, 169.

[9] F. C. Koch, E. M. Koch, and I. K. Ragins, *J. Biol. Chem.*, 1929, **85**, 141; H. B. Lemon, *ibid.*, p. 159; *A.*, 1930, 256, 257; R. Schönheimer, *Naturwiss.*, 1930, **18**, 881; *A.*, 1930, 1577.

[10] F. S. Spring, *J.*, 1930, 2664; *A.*, 219.

[11] *Annalen*, 1930, **482**, 264; *A.*, 1930, 1578.

[12] F. Reindel and E. Walter, *Annalen*, 1928, **460**, 212; I. M. Heilbron and W. A. Sexton, *J.*, 1929, 921; *A.*, 1928, 295; 1929, 809.

[13] F. Reindel, *Annalen*, 1928, **460**, 131; *A.*, 1928, 295.

[14] F. Reindel, E. Walter, and H. Rauch, *Annalen*, 1927, **452**, 34; I. M. Heilbron and F. S. Spring, *J.*, 1929, 2806; *A.*, 1927, 241; 1930, 210.

A significant observation is the production of a dibasic acid, $C_{25}H_{44}(CO_2H)_2$, when ergostanol (*allo*-α-ergostanol = hexahydro-ergosterol) is oxidised with chromic acid [13] to the ketone ergostanone. This acid when heated gives a ketone, $C_{26}H_{44}O$, by loss of carbon dioxide and water, which points to the rupture in the first place of a six- or seven-membered ring.

In connexion with vitamin-*D* the study of various isomerides of the sterol is of the greatest importance, and a large number of experiments in this direction have been recorded of which a short account will now be given. The changes in structure no doubt involve movements in position of the double bonds and changes in steric arrangement of more than one kind. The location of the points of unsaturation is a matter of difficulty, and the conclusions so far reached must be regarded as tentative.

Isomeric change in ergosterol was first brought about by the action of hydrogen chloride upon its acetate,[14] the product, ergosterol-*B* (*iso*ergosterol), being obtained in several stereoisomeric forms (ergosterols B_1, B_2, and B_3). The only effect here is an alteration in position of the double bonds or possibly conversion of a *cis*- into a *trans*-configuration with respect to a double bond in the side chain; [15] for the products all yield the same perhydro-derivative.

The addition of two atoms of hydrogen (sodium and alcohol) [16] and their removal at another point by means of mercuric acetate or perbenzoic acid [17, 19, 20] yields ergosterol-*D*: these operations in inverse order furnish ergosterol-*F*; [18] and yet another isomeride, ergosterol-*E*, has been described as resulting from the combination of these processes with the hydrogen chloride treatment.[19] A different series of compounds arises when the sterol is converted by mercuric acetate into its dehydro-derivative and this is subjected to the catalytic action of finely divided nickel at 220°.[20] The products, ergostatrienone-*D* and *u*-ergostatrienone, yield on reduction ergosterol-*D* and the new isomeride *u*-ergostatrienol.

In the study of the irradiation of ergosterol with ultra-violet

[15] A. Windaus, K. Dithmar, H. Murke, and F. Suckfüll, *Annalen*, 1931, **488**, 91; *A.*, 1051.

[16] A. Windaus and J. Brunken, *ibid.*, 1928, **460**, 225; *A.*, 1928, 424.

[17] A. Windaus and A. Lüttringhaus, *ibid.*, 1930, **481**, 119; *A.*, 1930, 1178.

[18] A. Windaus, W. Bergmann, and A. Lüttringhaus, *ibid.*, 1929, **472**, 195; A. Windaus, W. Bergmann, and H. Butte, *ibid.*, 1930, **477**, 268; *A.*, 1929, 1065; 1930, 338.

[19] I. M. Heilbron, F. Johnstone, and F. S. Spring, *J.*, 1929, 2248; *A.*, 1929, 1442.

[20] A. Windaus and E. Auhagen, *Annalen*, 1929, **472**, 185; *A.*, 1929, 1065.

light, two physiologically inactive sterols, suprasterols I and II, have been isolated besides the vitamin-*D*.[21]

Certain sterols undergo isomerisation when heated with sodium ethoxide in ethyl alcohol at 200°: this results in the production of *epi*-derivatives (in which the configuration of the >CH·OH group is inverted), hydrogenation of a double bond occurring to some extent at the same time.[15] Finally, the production of isomerides by successive dehydration and hydration [15] and by the action of benzoyl chloride, followed by hydrolysis (ergosterol-*C*),[20] has not yet been thoroughly investigated.

The isomerides *B*, *D*, *E* and *F* all retain their three double bonds and are reducible to ergostanol. Like ergosterol itself, they give insoluble addition compounds with digitonin. A second group of substances is not precipitated by digitonin, but is converted by heating with sodium ethoxide into members of the first group. They are reduced catalytically to *epi*ergostanol, the relationship of which to ergostanol is evident from their oxidation to the common ketone ergostanone. A third group, including *u*-ergosterol and the products of irradiation, is not precipitated by digitonin either at once or after heating with sodium ethoxide. These isomerides also still have three double bonds but on complete hydrogenation they yield neither ergostanol nor *epi*ergostanol. It is as yet uncertain whether the difference here is of a steric kind or one involving a change in the structure of the carbon skeleton.

A number of attempts have been made to define the exact positions of the double bonds in ergosterol and its isomerides, but this problem has not yet been solved. One argument [22] used is based on the similarity of the absorption spectra of ergosterol and of cholesterilene, $C_{27}H_{44}$, a dehydration product of cholesterol, but apart from the uncertainty of such evidence it cannot yet be claimed that the structure of this hydrocarbon has been determined beyond doubt. It may be taken as certain, however, that conjugated double bonds are present in ergosterol, dehydroergosterol, ergosterol-B_3, -*D*, and -*F*, dehydroergosterol, the two suprasterols, and vitamin-*D*—all of which combine with maleic anhydride.[23]

The isolation of the vitamin will no doubt lead to a still more rapid development of the chemistry of ergosterol and the further results will be awaited with great interest.

J. W. Baker.
G. M. Bennett.

[21] A. Windaus, J. Gaede, J. Köser, and G. Stein, *Annalen*, 1930, **483**, 17; *A.*, 1577.

[22] I. M. Heilbron, R. A. Morton, and W. A. Sexton, *J.*, 1928, **48**, 347; A. C. Bose and W. Doran, *J.*, 1929, 2244; *A.*, 1928, 219, 410; 1929, 1432.

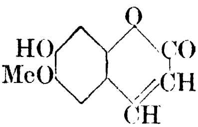
[23] A. Windaus and A. Lüttringhaus, *Ber.*, 1931, **64**, [*B*], 850; *A.*, 840.

PART III.—HETEROCYCLIC DIVISION.

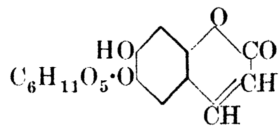
Oxygen Ring Compounds.

THE past year has produced another crop of important developments in the chemistry of those natural products which contain an oxygen atom as part of a heterocyclic system.

Although previous investigations have made it clear that scopoletin, which has been isolated from several different natural sources, has the structure (I), its synthesis [1] from 2 : 4-dihydroxyanisole is not without interest. The latter compound was transformed first into 2 : 4-dihydroxy-5-methoxybenzaldehyde (II) by condensation with hydrogen cyanide in ether in the presence of zinc cyanide and hydrogen chloride, and then into *O*-acetylscopoletin by heating with


(I.)


(II.)


(III.)

sodium acetate and acetic anhydride. Hydrolysis led to scopoletin, identical with the naturally occurring substance. A similar series of reactions starting from 2 : 5-dihydroxyanisole led to 6-hydroxy-7-methoxycoumarin (æsculetin monomethyl ether).[2] The latter proved to be identical with the product derived from the hydrolysis of æsculin methyl ether, so that the position assigned to the glucose residue in æsculin [3] (III) is thus confirmed.

The problem of determining the exact positions occupied by the hydroxyl or methoxyl groups in natural products belonging to the flavone and related types is frequently one of great difficulty, largely because the synthetical methods employed are not always free from ambiguity. Considerable doubt has recently existed concerning the validity of the formulæ previously assigned to baicalein and wogonin, two flavones which have been isolated from the roots of *Scutellaria baicalensis*. The view that baicalein is 5 : 6 : 7-trihydroxyflavone [4] (IV) rested upon the fact that it is apparently identical with the compound obtained by G. Bargellini [5]

[1] F. S. H. Head and A. Robertson, *J.*, 1931, 1241; R. Seka and P. Kallir, *Ber.*, 1931, **64**, [*B*], 909; *A.*, 737.

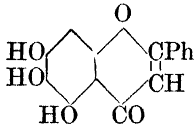
[2] R. Seka and P. Kallir, *ibid.*, p. 622; *A.*, 606.

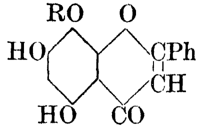
[3] F. S. H. Head and A. Robertson, *J.*, 1930, 2434; *Ann. Reports*, 1930, **27**, 178.

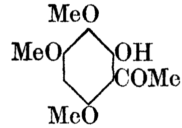
[4] K. Shibata, S. Iwata, and M. Nakamura, *Acta Phytochim.*, 1923, **1**, 105; *A.*, 1923, i, 591.

[5] *Gazzetta*, 1919, **49**, ii, 47; *A.*, 1919, i, 545.

by the action of hydriodic acid on 2 : 3 : 4 : 6-tetramethoxy-ω-benzoylacetophenone. The constitution accorded to Bargellini's


(IV.)

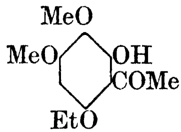
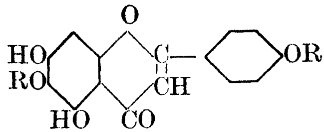

(V.)


(VI.)

product, for which there were at first two alternatives, depended, however, upon the fact that it differed from a hydroxychrysin which had been regarded [6] as 5 : 7 : 8-trihydroxyflavone (V; R = H). Wogonin (a dihydroxymethoxyflavone) has been demethylated to a trihydroxyflavone which is not identical with baicalein, and its dimethyl ether was found to be different from baicalein trimethyl ether.[7] Furthermore, by heating 2 : 3 : 4 : 6-tetramethoxyacetophenone with aluminium chloride and treating the product—supposed to be 2-hydroxy-3 : 4 : 6-trimethoxyacetophenone (VI)—with benzoic anhydride and sodium benzoate, wogonin dimethyl ether was obtained. Wogonin has been regarded, therefore, as 5 : 7-dihydroxy-8-methoxyflavone (V; R = Me). It has become apparent, however, that hydroxychrysin cannot be 5 : 7 : 8-trihydroxyflavone, and, furthermore, the evidence for the structures assigned to baicalein and wogonin became less sound when it was reported a few months ago [8] that the substance (VI) was in reality 6-hydroxy-2 : 3 : 4-trimethoxyacetophenone. More recently, however, it has transpired that the latter observation was unsound, and further work [9] has now confirmed the nature of (VI) and established definitely the structures of the natural products. Antiarol (3 : 4 : 5-trimethoxyphenol) was transformed into its ethyl ether and then converted into 2-hydroxy-3 : 4-dimethoxy-6-ethoxyacetophenone (VII) by the action of acetyl chloride and aluminium chloride. The position of the hydroxyl group was confirmed by the coloration which is developed with ferric chloride. After treatment with benzoic anhydride and sodium benzoate, followed by de-alkylation, 5 : 7 : 8-trihydroxyflavone was obtained. It proved to be identical with the demethylation product of wogonin, and it necessarily follows that baicalein is correctly represented by the formula (IV). A re-investigation of Bargellini's synthesis of the latter substance has indicated, however, that it is by no means as

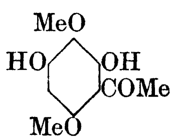
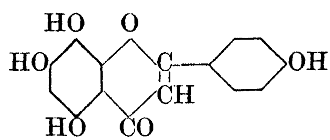
[6] M. Nierenstein, *Ber.*, 1912, **45**, [*B*], 499.
[7] S. Hattori, *Acta Phytochim.*, 1930, **5**, 99; *A.*, 493.
[8] K. Shibata and S. Hattori, *J. Pharm. Soc. Japan*, 1931, **51**, 15; *Chem. Zentr.*, 1931, i, 3358.
[9] S. Hattori, *Acta Phytochim.*, 1931, **5**, 219.

satisfactory as it appeared to be, for it has been reported [10] that the reaction leads more frequently to the isomeric 5 : 7 : 8-trihydroxyflavone. Similarly the action of hydriodic acid on 2 : 3 : 4 : 6-

(VII.)   (VIII.)

tetramethoxy-ω-anisoylacetophenone, which Bargellini [11] has employed for the synthesis of scutellarein (VIII; R = H), is stated to yield mainly 5 : 7 : 8 : 4′-tetrahydroxyflavone, the structure of which was confirmed by the anisoylation and subsequent demethylation of (VI). Further confirmation for the structure assigned to baicalein is derived from the fact that its trimethyl ether yields antiarol, in addition to benzoic acid and acetophenone, when boiled with aqueous potassium hydroxide for several hours.

It has recently been reported [12] that the anisoylation of 2 : 4-dihydroxy-3 : 6-dimethoxyacetophenone (IX) proceeds normally and that the product obtained on subsequent demethylation is 5 : 7 : 8 : 4′-tetrahydroxyflavone (X). These observations are incompatible with earlier statements [13] to the effect that the reaction takes an unexpected course resulting in partial demethylation and the formation of (VIII; R = Me), and the ultimate synthesis, on

(IX.)   (X.)

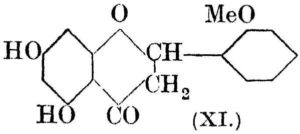
further demethylation, of scutellarein. Fortunately the constitution assigned to scutellarein is not involved in this ambiguity, since alternative syntheses have been developed.

The structure allotted to citronetin, a compound obtained by the hydrolysis of the glucoside citronin, has been confirmed [14] by the use of a reaction which has previously been employed for synthesising flavanones.[15] The action of *o*-methoxycinnamoyl chloride on phloroglucinol in nitrobenzene in the presence of aluminium chloride yielded, among other substances, 5 : 7-di-

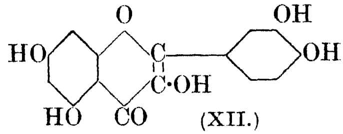
[10] S. Hattori, *loc. cit.*
[11] *Gazzetta*, 1915, **45**, 69; *A.*, 1915, i, 84.
[12] S. Furukawa and H. Tamaki, *Chem. Zentr.*, 1931, ii, 2161.
[13] F. Wessely and G. H. Moser, *Monatsh.*, 1930, **56**, 97; *Ann. Reports*, 1930, **27**, 174.
[14] J. Shinoda and S. Sato, *Chem. Zentr.*, 1931, ii, 2326.
[15] See *Ann. Reports*, 1928, **25**, 169.

hydroxy-2′-methoxyflavanone (XI), which proved to be identical with the natural product.

Further interesting observations have been made regarding the conversion of quercetin (XII) into cyanidin (XIII). Thus, while the action of sodium amalgam in alkaline solution on quercetin pentamethyl ether leads readily to the pseudo-base of pentamethyl-



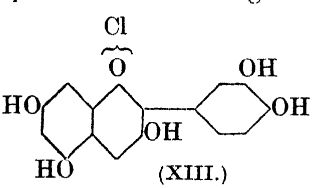
(XI.)



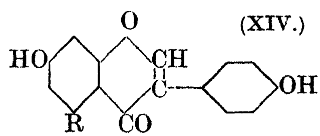
(XII.)

cyanidin, quercetin itself gives a negligible quantity of cyanidin. That the failure of the process under these conditions is due to the presence of the free hydroxyl group in the 3-position is made probable by the fact that a good yield of cyanidin chloride is obtained when similar treatment is applied to rutin (a rhamnoglucoside of quercetin with the sugar residue in the 3-position) and the reaction mixture is heated with hydrochloric acid.[16] It has also been reported [17] that a small yield of pentamethylcyanidin chloride can be obtained by the reduction of quercetin pentamethyl ether with titanium trichloride in methyl-alcoholic ammonia.

Of considerable interest is the isolation of several *iso*flavone glucosides from the soya bean.[18] One of these, which has been called " genistin," yielded, on hydrolysis, glucose and the previously known genistein (XIV; R = OH). The constitution of the glucose-free product was indicated not only by the properties of its simple derivatives, but also by alkali fission into formic acid, phloroglucinol, and *p*-hydroxyphenylacetic acid. An examination of the product derived from the hydrolysis of the methylated glucoside showed that it was 7-hydroxy-5 : 4′-dimethoxy*iso*flavone, from which it follows that the glucose residue in genistin is in the 7-position. A second glucoside, daidzin, has given glucose and a



(XIII.)



(XIV.)

hitherto unknown *iso*flavone (XIV; R = H) to which the name " daidzein " has been given. Alkaline hydrolysis of the latter

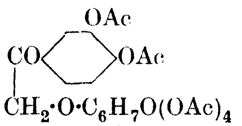
[16] Y. Asahina and M. Inubuse, *Ber.*, 1931, **64**, [*B*], 1256; *A.*, 940.

[17] P. Karrer, Y. Yen, and I. Reichstein, *Helv. Chim. Acta*, 1930, **13**, 1308; *A.*, 233.

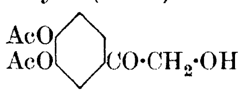
[18] E. Walz, *Annalen*, 1931, **489**, 118.

yielded formic acid and 2 : 4-dihydroxyphenyl *p*-hydroxybenzyl ketone, the identity of which was established by its synthesis from resorcinol and *p*-hydroxyphenylacetonitrile by means of a Hoesch reaction. The glucose residue is again attached in the 7-position, since the methylated glucoside, on hydrolysis in two stages, gave 2 : 4-dihydroxyphenyl *p*-methoxybenzyl ketone. At least one other *iso*flavone glucoside has been isolated from the same source, but the exact positions of the substituents in the glucose-free material have not yet been determined.

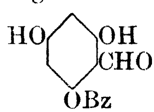
The earlier applications of the anthocyanidin syntheses of Pratt and Robinson to substances containing the glucose residue, culminating in the synthesis of callistephin chloride,[19] foreshadowed the preparation of other flower pigments, and further extensive work in this field has now been described. The acetylated β-glucoside (XV), from the action of dry silver carbonate on *O*-tetra-acetyl-α-glucosidyl bromide and ω-hydroxy-3 : 4-diacetoxyacetophenone (XVI) in chloroform solution, has been treated in chloroform–ether with *O*-benzoylphloroglucinaldehyde (XVII) and dry hydrogen chloride.



(XV.)

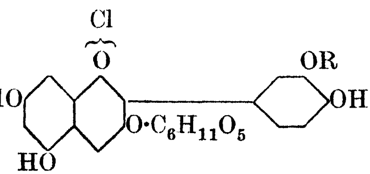


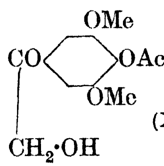
(XVI.)



(XVII.)

The resulting flavylium salt, on hydrolysis with aqueous sodium hydroxide and subsequent acidification with hydrochloric acid, yielded 3-β-glucosidylcyanidin chloride [20] (XVIII; R = H), which proved to be identical with a specimen of chrysanthemin chloride from the flowers of the deep-red chrysanthemum. By a similar series of reactions *O*-benzoylphloroglucinaldehyde and the tetra-acetylglucoside of the ω-hydroxy-ketone (XIX) ultimately gave 3-β-glucosidylmalvidin chloride [21] (XX), which was shown to be

(XVIII.)




(XIX.)

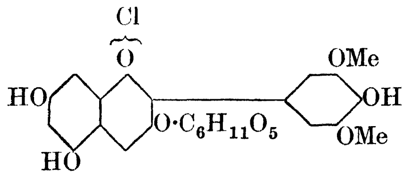
identical with œnin chloride, an anthocyanin from the skins of purple-black grapes. Furthermore, 3-β-glucosidylpeonidin chloride [22] (XVIII; R = Me), from the tetra-acetylglucoside of ω-hydr-

[19] See *Ann. Reports*, 1928, **25**, 166.
[20] S. Murakami, A. Robertson, and R. Robinson, *J.*, 1931, 2665.
[21] L. F. Levy, T. Posternack, and R. Robinson, *ibid.*, p. 2701.
[22] L. F. Levy and R. Robinson, *ibid.*, p. 2715.

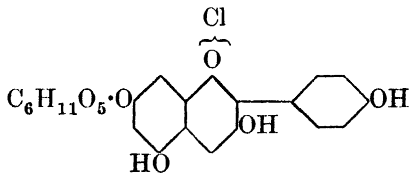
oxy-4-acetoxy-3-methoxyacetophenone and *O*-benzoylphloroglucinaldehyde, was found to be identical with oxycoccicyanin chloride, a pigment of American cranberries.[23] The galactoside obtained by the action of dry silver carbonate on ω-hydroxy-3 : 4-diacetoxyacetophenone and *O*-tetra-acetyl-α-galactosidyl bromide has been converted by a similar process into 3-β-galactosidylcyanidin chloride[24] (XVIII; R = H; $C_6H_{11}O_5$ = galactose residue), which is apparently identical with natural idæin chloride.

These synthetical methods have been further extended to the preparation of several flavylium salts with a sugar residue in other

(XX.)

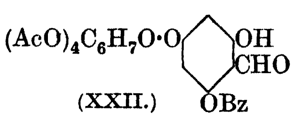


than the 3-position.[25] For example, 7-β-glucosidylpelargonidin chloride (XXI) was obtained from ω : 4-dihydroxyacetophenone

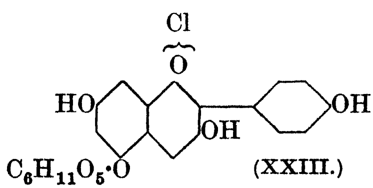


(XXI.)

and the tetra-acetyl-β-glucoside (XXII), while a related series of reactions gave ultimately 5-β-glucosidylpelargonidin chloride (XXIII), which was found to be identical with pelargonenin chloride derived from the partial hydrolysis of pelargonin chloride.



(XXII.)



(XXIII.)

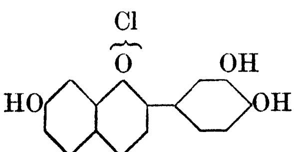
The definite characterisation of many of these glucosides has revealed several very interesting generalisations. For instance, the presence of a free hydroxyl group in the 3-position renders the

[23] (Miss) K. E. Grove and R. Robinson, *Biochem. J.*, 1931, **25**, 1706.

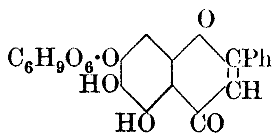
[24] (Miss) K. E. Grove and R. Robinson, *J.*, 1931, 2722.

[25] A. León, A. Robertson, R. Robinson, and T. R. Seshadri, *ibid.*, p. 2672; L. F. Levy and R. Robinson, *ibid.*, p. 2738.

molecule very susceptible to attack by oxidising agents,[26] so that such compounds rapidly decolourise dilute solutions of ferric chloride. Thus, for example, the yellow-brown colour of a very dilute ferric chloride solution was comparatively rapidly discharged by pelargonidin chloride and its 4′-, 5-, and 7-β-glucosides, but was unchanged by callistephin chloride (3-β-glucosidylpelargonidin chloride), 3-β-glucosidylpeonidin chloride (XVIII; R = Me), and luteolinidin chloride [27] (XXIV) after a much greater period of time. Analogous important generalisations can be drawn from a study of the distribution of these substances between amyl alcohol and dilute hydrochloric acid, and also from a careful examination of their colour reactions in a range of buffered solutions of graded p_H.[28] With the aid of these characteristic features it is possible to make far-reaching deductions concerning the structures of other naturally occurring anthocyanins. For instance, cyanin, pelargonin, peonin, and malvin have hitherto been considered to be 5-biosides, but, since there are now clear indications that there are sugar residues in both the 3- and the 5-position, these anthocyanins must be regarded as 3 : 5-diglucosides. On the other hand, mecocyanin, prunicyanin, and keracyanin are biosides with the sugar group in the 3-position.[29] Furthermore, the colour reactions, etc., of the anthocyanins and anthocyanidins have been made the basis of methods for examining and detecting the nature of the anthocyanins present in numerous



(XXIV.)



(XXV.)

flowers.[30] A very interesting outcome of the latter investigation is the observation that the colours of these salts can be modified to a remarkable degree by the presence of other substances (co-pigments) which apparently form with them weak additive complexes. The actual colours of the flowers themselves may depend to a considerable extent upon this factor.

Other investigations among natural products belonging to the oxygen ring types have included studies into the position of the sugar group in a few miscellaneous glycosides. Baicalin, from the

[26] Compare P. Karrer, R. Widmer, A. Helfenstein, W. Hürliman, O. Nievergelt, and P. Monsarrat-Thomas, *Helv. Chim. Acta*, 1927, **10**, 729.

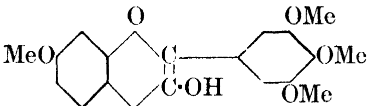
[27] A. León and R. Robinson, *J.*, 1931, 2732.

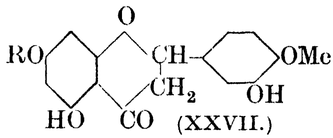
[28] Compare A. Robertson and R. Robinson, *Biochem. J.*, 1929, **23**, 35.

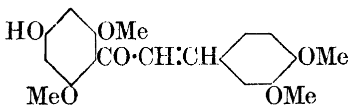
[29] (Mrs.) G. M. Robinson and R. Robinson, *Nature*, 1931, **128**, 413.

[30] (Mrs.) G. M. Robinson and R. Robinson, *Biochem. J.*, 1931, **25**, 1687.

roots of *Scutellaria baicalensis*, yields glycuronic acid and baicalein (5 : 6 : 7-trihydroxyflavone) on hydrolysis, and it has now been shown [31] that the glycuronic acid residue is in the 7-position (formula XXV) from a comparison of the reactions of baicalin with those of primetin (5 : 6-dihydroxyflavone). Thus it gives a monomethyl ether which develops a violet-brown colour with ferric chloride, indicative of a free hydroxyl group in the 5-position. Furthermore, baicalin itself, like primetin, gives a green colour with ferric chloride, and is very readily oxidised. It has been concluded [32] that the product obtained from myricitrin, a rhamnoside of myricetin (5 : 7 : 3′ : 4′ : 5′-pentahydroxyflavonol), by methylation and subsequent hydrolysis is myricetin 5 : 7 : 3′ : 4′ : 5′-pentamethyl ether (XXVI), from which it follows that the sugar residue, as in several other flavonol glycosides, is in the 3-position. The bioside hesperidin, which yields rhamnose, glucose, and hes-


(XXVI.)


(XXVII.)

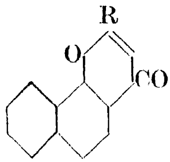
(XXVIII.)


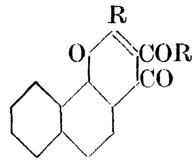
peritin (XXVII; R = H) on hydrolysis, has been shown [33] to have the biose residue in the 7-position (XXVII; R = $C_{12}H_{21}O_9$). On methylation and subsequent hydrolysis it gave 4-hydroxy-2 : 6-dimethoxyphenyl 3 : 4-dimethoxystyryl ketone (XXVIII) (the flavanone structure readily isomerises to the chalkone), which has been synthesised by the interaction of veratraldehyde and 4-hydroxy-2 : 6-dimethoxyacetophenone.

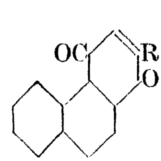
Many interesting and important investigations of the methods used for the synthesis of chromones and coumarins have recently been described. The extremely valuable reaction whereby the acylation of certain polyhydroxyacetophenone derivatives leads to the production of several chromone types [34] cannot be used with *o*-hydroxyacetophenone itself. It has now been found,[35] however, that the process can be applied to 2-acetyl-1-naphthol. 1 : 4-α-Naphthapyrones (I) result from the action of a mixture of the

[31] K. Shibata and S. Hattori, *Acta Phytochim.*, 1930, **5**, 117; *A.*, 493.
[32] S. Hattori and K. Hayashi, *ibid.*, 1931, **5**, 213.
[33] F. E. King and A. Robertson, *J.*, 1931, 1704.
[34] See *Ann. Reports*, 1929, **26**, 152.
[35] A. S. Bhullar and K. Venkataraman, *J.*, 1931, 1165.

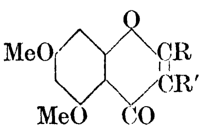
anhydride and alkali salt of the appropriate acid upon this compound, but the simultaneous formation of the 3-acyl derivatives (II)

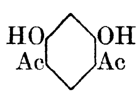

(I.)

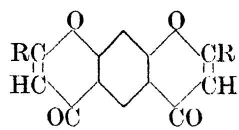

(II.)

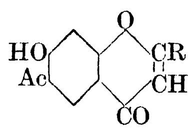

(III.)

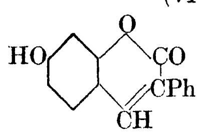
is a marked feature of the process, whereas analogous carbon-acylation is very rare in the aforementioned benzene series. The reaction can also be applied to 1-acetyl-2-naphthol with the formation of 1 : 4-βα-naphthapyrones[36] (III); simultaneous carbon-acylation again occurs when acetic anhydride is used. Further examples of this reaction involving the use of simpler hydroxy-ketones have been described.[37] By acylation of 2-hydroxy-4 : 6-dimethoxypropiophenone and 2-hydroxy-4 : 6-dimethoxy-*n*-butyrophenone, for example, chromones of the type (IV) have been prepared. Acetylation of 2-hydroxy-4 : 6-dimethoxyacetophenone under vigorous conditions gave a product, believed to be (IV; R = Me; R′ = Ac), in which acetylation in the 3-position has apparently taken place. A further extension[38] of the reaction to the acylation of 4 : 6-diacetylresorcinol (V) has yielded the dichromones (VI) and the chromones (VII).


(IV.)


(V.)


(VI.)

(VII.)



(VIII.)

The condensation of phenols with β-ketonic esters has been extensively employed for the synthesis of both coumarins and chromones. It has previously been considered that, in general, the former result when sulphuric acid is used as the condensing agent, and the latter in the presence of phosphoric oxide. More recent studies[37, 39] of the reaction have shown, however, that while the

[36] B. K. Menon and K. Venkataraman, *J.*, 1931, 2591.

[37] F. W. Canter, F. H. Curd, and A. Robertson, *ibid.*, pp. 1245, 1255; F. W. Canter, A. R. Martin, and A. Robertson, *ibid.*, p. 1877.

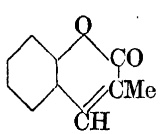
[38] K. C. Gulati and K. Venkataraman, *ibid.*, p. 2376.

[39] D. Chakravarti, *J. Indian Chem. Soc.*, 1931, **8**, 129, 407; *A.*, 962, 1304; A. Robertson, W. F. Sandrock, and Miss C. B. Hendry, *J.*, 1931, 2426.

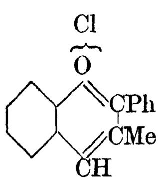
use of sulphuric acid always leads to the formation of coumarins, when this is replaced by phosphoric oxide, the nature of the product depends upon the particular phenol which is employed. Thus, although simple monohydric phenols and quinol yield chromones, resorcinol, orcinol, pyrogallol, phloroglucinol, phloroglucinol dimethyl ether, and α-naphthol give coumarins. The course of the reaction is apparently independent of the nature of the β-ketonic ester.

An investigation [40] of the condensation of α-formylphenylacetonitrile, CHO·CHPh·CN, and benzoyloxymethylenephenylacetonitrile, CH(O·COPh)⁚CPh·CN, with polyhydric phenols in dry ether in the presence of zinc chloride and hydrogen chloride has made it clear that the reaction leads, in general, to the corresponding derivatives of 3-phenylcoumarin and not to the isomeric *iso*flavones (3-phenylchromones). For instance, the use of resorcinol results in the formation of 7-hydroxy-3-phenylcoumarin (VIII). The condensation, which involves the interaction of the cyano-group and a phenolic hydroxyl group, is interesting, therefore, because it does not follow the normal course of the Hoesch reaction.

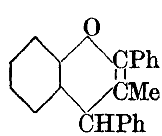
It is possible in the space available to mention only a very few of the more outstanding of the remaining points in the year's output of work on oxygen ring compounds. Coumarins substituted in the 3-position can readily be converted by treatment with phenylmagnesium bromide in dilute solution at room temperature into the corresponding 2-phenylbenzopyrylium salts (*e.g.*, X from IX), but, when the reaction is carried out in hot concentrated solution, the 2 : 4-diphenyl-Δ^2-chromens (*e.g.*, XI) are formed.[41] The former



(IX.)



(X.)



(XI.)

reaction, however, gives only poor yields of the benzopyrylium salts when applied to coumarins substituted in the 4-position, but the more vigorous conditions lead readily to the production of 2 : 2-diphenyl-Δ^3-chromens (XII).

Of some interest is the observation [42] that coumarone and diphenyl-

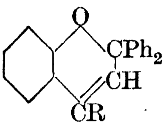
[40] I. C. Badhwar, W. Baker, B. K. Menon, and K. Venkataraman, *J.*, 1931, 1541.

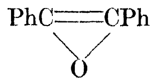
[41] I. M. Heilbron and D. W. Hill, *J.*, 1927, 2005; I. M. Heilbron, D. W. Hill, and H. N. Walls, *J.*, 1931, 1701.

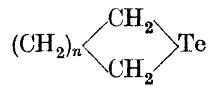
[42] N. A. Orlov and V. V. Tistschenko, *Ber.*, 1930, **63**, [*B*], 2948; *A.*, 233.

ene oxide are formed in good yields when the vapours of coumarin and xanthone respectively are submitted at atmospheric pressure to temperatures of 860—880°. Open-chain ketones do not lose carbon monoxide to give simple products under similar conditions.

The recent preparation of derivatives of acetylene oxide, in which there is an unsaturated 3-membered oxygen ring, is a noteworthy feature in this field. These substances resulted in poor yields by reactions analogous to those which lead to the ethylene oxides. The action of powdered potassium hydroxide on desyl

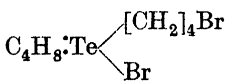

(XII.)

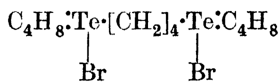

(XIII.)


(XIV.)

chloride, CHPhCl·COPh, in toluene has given the diphenyl derivative (XIII), while the monophenyl compound has been obtained from phenacyl bromide by the use of silver oxide.[43] The products were found to be comparatively stable, but gave desyl chloride and phenacyl chloride respectively when heated for two hours with concentrated hydrochloric acid at 120°.

The preparation of *cyclo*tellurobutane (tetrahydrotellurophen) (XIV; $n = 2$) by a process essentially similar to that previously used for the synthesis of *cyclo*telluropentane[44] (XIV; $n = 3$) has been described.[45] The action of aluminium telluride on αδ-tetra-

(XV.) 

 (XVI.)

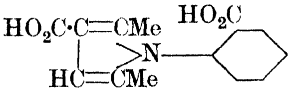
methylene dibromide led to a mixture of the telluronium salts (XV) and (XVI), which dissociated, on heating, to give tetramethylene dibromide and *cyclo*tellurobutane. A more convenient procedure was found by dissolving amorphous tellurium in αδ-tetramethylene di-iodide at 130°. The *cyclo*telluributane 1 : 1-di-iodide, $C_4H_8{:}TeI_2$, which was formed was reduced by passing sulphur dioxide through its suspension in boiling water. *cyclo*Tellurobutane exhibited the additive properties characteristic of the saturated cyclic telluro- and seleno-hydrocarbons.

5-*Membered Nitrogen Ring Compounds.*

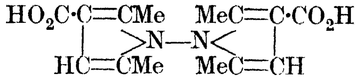
A noteworthy feature of the chemistry of pyrrole derivatives is the recent resolution of 1-*o*-carboxyphenyl-2 : 5-dimethylpyrrole-

[43] W. Madelung and M. E. Oberwegner, *Annalen*, 1931, **490**, 201.
[44] See *Ann. Reports*, 1928, **25**, 196.
[45] G. T. Morgan and F. H. Burstall, *J.*, 1931, 180.

3-carboxylic acid[46] (I) and 2 : 5 : 2′ : 5′-tetramethyl-1 : 1′-dipyrryl-3 : 3′-dicarboxylic acid[47] (II) into optically active components. It



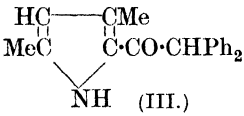
(I.)



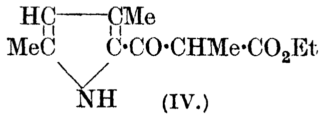
(II.)

is probable that the activity of these compounds is due to restricted rotation similar to that observed in the diphenyl series, although it is just possible that its origin may lie in the asymmetric nitrogen atoms.

The action of aliphatic diazo-compounds on pyrroles may pursue various courses.[48] The use of diazoacetic ester has been found to result in the introduction of the $\cdot CH_2\cdot CO_2Et$ group into the nucleus at an α-carbon atom, if this is available, but diazo-ketones and diazo-ketonic esters react differently. For instance, benzoylphenyldiazomethane and 2 : 4-dimethylpyrrole yielded the product (III), which has apparently resulted from the intermediate formation of diphenylketen. In fact, the latter substance has been shown to add directly to 2 : 4-dimethylpyrrole with the formation of (III).



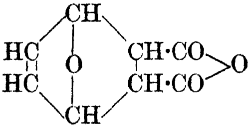
(III.)



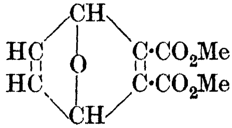
(IV.)

Similarly, diazoacetoacetic ester and 2 : 4-dimethylpyrrole reacted together to give the compound (IV). Ketens and *iso*cyanic esters are stated to combine additively with pyrroles with the formation of ketones and amides respectively.

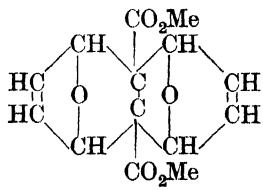
Very interesting results have also been obtained by O. Diels, K. Alder, and their collaborators in an extension of their study of additive processes to certain heterocyclic systems. Furan behaved



(V.)



(VI.)



(VII.)

in a manner similar to that observed in unsaturated carbocyclic systems, and with maleic anhydride yielded the product[49] (V).

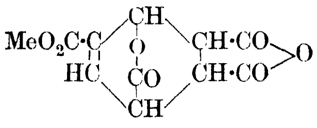
[46] L. H. Bock and R. Adams, *J. Amer. Chem. Soc.*, 1931, **53**, 374; *A.*, 362.

[47] C. Chang and R. Adams, *ibid.*, p. 2353; *A.*, 1074.

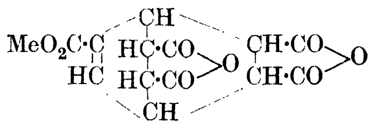
[48] C. D. Nenitzescu and E. Solomonica, *Ber.*, 1931, **64**, [*B*], 1924; *A.*, 1305.

[49] O. Diels, K. Alder, and E. Naujoks, *Ber.*, 1929, **62**, [*B*], 554; *A.*, 1929, 570.

With dimethyl acetylenedicarboxylate it gave a similar substance (VI) besides a compound (VII) derived from the further addition of a second molecule of furan.[50] In the α-pyrone series similar additive reactions have been realised. Thus methyl coumalate gave with maleic anhydride in boiling toluene the product (VIII), but in boiling xylene the reaction proved to be rather more complex and led to (IX).[51] In the pyrrole series, however, the additive

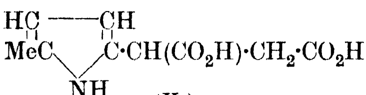


(VIII.)

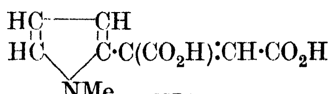


(IX.)

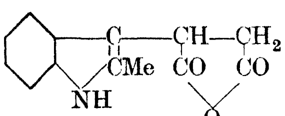
processes are of a different character and do not result in the formation of polycyclic derivatives. The main reactions are illustrated by the addition of maleic acid to 2-methylpyrrole with the formation of (X), or of acetylenedicarboxylic acid to 1-methylpyrrole with the production of (XI).[52] Certain indole derivatives closely resemble the pyrroles in this respect, but the reactions may also be more



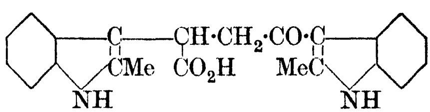
(X.)



(XI.)



(XII.)



(XIII.)

complex. For example, 2-methylindole and maleic anhydride gave not only (XII) but a further reaction product (XIII).[53] In the case of indole and 3-methylindole the course of the reaction was complicated by the primary polymerisation of the indole.

The tendency for the 2 : 3-linkage in the indole skeleton to combine additively with OH and NO_2, or 2OH, which is such a marked feature of the action of nitric acid on the *N*-acyl derivatives of tetrahydrocarbazole (XIV; $n = 2$) and dihydropentindole (XIV; $n = 1$), has been found to be enormously diminished when this

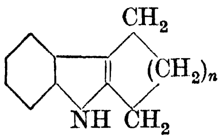
[50] O. Diels, K. Alder, H. Nienburg, and (Frl.) O. Schmalbeck, *Annalen*, 1931, **490**, 243.

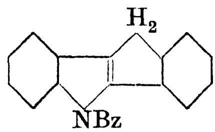
[51] O. Diels, K. Alder, and K. Müller, *ibid.*, p. 257.

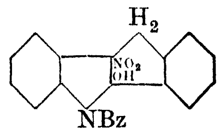
[52] O. Diels, K. Alder, and D. Winter, *ibid.*, 1931, **486**, 211; *A.*, 849; O. Diels, K. Alder, and H. Winckler, *ibid.*, 1931, **490**, 267.

[53] O. Diels, K. Alder, and W. Lübbert, *ibid.*, p. 277.

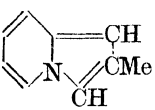
system is contained in more complex polycyclic types.[54] Thus, of many compounds investigated, only one, *viz.*, 7-benzoylbenzopentindole (XV), was found to give an addition product (XVI) of the kind mentioned.

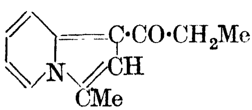

(XIV.)

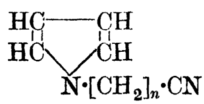

(XV.)


(XVI.)

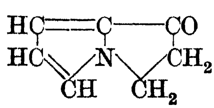
The synthesis of certain compounds in which a nitrogen atom is common to two fused ring systems is of considerable interest in view of the probable occurrence of similar structures in some alkaloids, *e.g.*, lupinine. When the addition product obtained from 2-methylpyridine and bromoacetone was distilled in steam in the presence of sodium hydrogen carbonate, 2-methylpyrrocoline (XVII) was obtained,[55] and the reaction has been applied to other analogous cases. Pyrrocolines have also been reported from the action of acid anhydrides on 2-methylpyridine, *e.g.*, 1-propionyl-3-methyl-

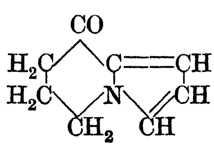

(XVII.)

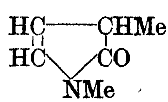

(XVIII.)


(XIX.)

pyrrocoline (XVIII) when propionic anhydride was used.[56] In addition, potassium pyrrole has been treated [57] with β-cyanoethyl toluene-*p*-sulphonate, and the 1-β-cyanoethylpyrrole (XIX; $n = 2$) so obtained made to undergo a Hoesch reaction with the formation of 3-keto-4 : 5-dihydrodi-(1 : 2)-pyrrole (XX). Similarly, γ-1-pyrrylbutyronitrile (XIX; $n = 3$), from the interaction of potassium pyrrole and γ-bromobutyronitrile, yielded 8-keto-5 : 6 : 7 : 8-tetrahydropyrrocoline (XXI).


(XX.)


(XXI.)


(XXII.)

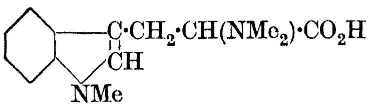
[54] S. H. Oakeshott and S. G. P. Plant, *J.*, 1928, 1840; S. A. Bryant and S. G. P. Plant, *J.*, 1931, 93.

[55] A. E. Tschitschibabin, *Ber.*, 1927, **60**, [*B*], 1607; *A.*, 1927, 885.

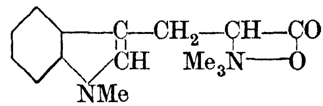
[56] A. E. Tschitschibabin and F. N. Stepanov, *Ber.*, 1930, **63**, [*B*], 470; *A.* 1930, 619.

[57] G. R. Clemo and G. R. Ramage, *J.*, 1931, 49.

Turning to natural products of the indole type, it is of interest to record that an examination [58] of the basic substances which can be extracted from toad secretions goes to show that bufotenine, for which the structure (XXII) has previously been suggested,[59] is an indole derivative of the formula (XXIII), while bufotenidine is the related betaine (XXIV). When calycanthine, an alkaloid from



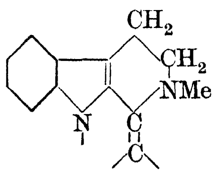
(XXIII.)

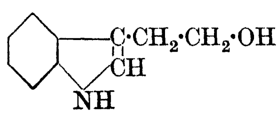


(XXIV.)

Calycanthus glaucus, was first benzoylated, and then either oxidised with potassium permanganate or treated with alkali, it yielded benzoyl-*N*-methyltryptamine, the constitution of which was established by its preparation from tryptamine (3-β-aminoethylindole) by the action of an excess of methyl iodide and subsequent benzoylation. On the basis of these results [60] it has been suggested that the alkaloid is a β-carboline derivative containing the group (XXV).

(XXV.)





(XXVI.)

It may also be mentioned that tryptophol (XXVI), derived from the action of yeast on tryptophan, has recently been synthesised [61] by the reduction of ethyl indolyl-3-acetate with sodium and alcohol.

Work dealing with glyoxaline derivatives and published during the past two years includes the synthesis [62] of *l*-2-thiolhistidine (IV). This is of special interest in view of the close relationship between this compound and several natural substances, and of the probability that it may itself be found among the products of the hydrolysis of proteins. Natural *l*-histidine (I) was converted first into its methyl ester dihydrochloride and then, by benzoylation, into methyl αγδ-tribenzamido-Δ^{γ}-pentenoate (II), which, with methyl-alcoholic hydrogen chloride, gave methyl αδ-dibenzamido-γ-ketovalerate (III). The dihydrochloride of the corresponding αδ-diamino-γ-ketovaleric acid, obtained by boiling with 20%

[58] H. Wieland, G. Hesse, and H. Mittasch, *Ber.*, 1931, **64**, [*B*], 2099; *A.*, 1310.

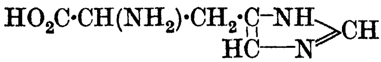
[59] H. Handovsky, *A.*, 1920, i, 495.

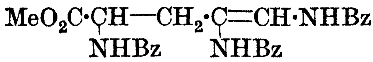
[60] R. H. F. Manske, *Canadian J. Res.*, 1931, **4**, 275; *A.*, 855.

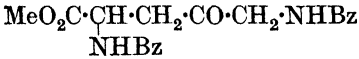
[61] R. W. Jackson, *J. Biol. Chem.*, 1930, **88**, 659; *A.*, 97.

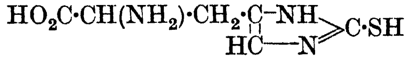
[62] J. N. Ashley and C. R. Harington, *J.*, 1930, 2586.

hydrochloric acid, yielded, on treatment with one molecular equivalent of sodium thiocyanate, the monohydrochloride of *l*-2-thiol-


(I.)


(II.)

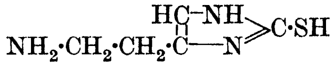

(III.)

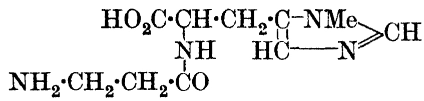

(IV.)

histidine (IV). The preparation of 2-thiolhistamine [63] (V) by the interaction of αδ-diamino-β-ketobutane dihydrochloride,

$$HCl,NH_2\cdot CH_2\cdot CO\cdot CH_2\cdot CH_2\cdot NH_2,HCl,$$

and sodium thiocyanate is closely related to the above synthesis. It is noteworthy that this substance does not show to any appreciable extent the physiological properties of histamine.


(V.)


(VI.)

Among the naturally occurring glyoxalines, anserine, recently isolated from bird muscle-tissue,[64] has been shown to have the constitution (VI).[65] Thus it yielded, on hydrolysis with baryta, β-aminopropionic acid and an *N*-methyl derivative of *dl*-histidine. The relative positions of the side-chain and methyl group were indicated by the fact that anserine gave 1 : 5-dimethylglyoxaline when distilled with soda-lime. Anserine differs from the closely related carnosine only in having the methyl group attached to the nitrogen atom of the glyoxaline ring. When the hydrolysis is effected by the use of 20% sulphuric acid for 6—8 hours, these products yield *l*-methylhistidine and *l*-histidine respectively.[66]

Of interest is the preparation of 1 : 2-diphenylglyoxalino-4 : 5(3′ : 2′)-quinoline [67] (VII). This was accomplished by first heating the azlactone (VIII), from the condensation of *o*-nitrobenzaldehyde with hippuric acid, with aniline in the presence of copper powder to obtain *o*-nitrobenzylidenebenzamidoacetanilide

[63] F. L. Pyman, *J.*, 1930, 98.

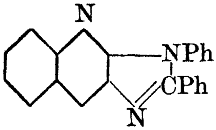
[64] D. Ackermann, O. Timpe, and K. Poller, *Z. physiol. Chem.*, 1929, **183**, 1; *A.*, 1929, 944.

[65] W. Linneweh, A. W. Keil, and F. A. Hoppe-Seyler, *ibid.*, p. 11; *A.*, 1929, 944; F. L. Pyman, *J.*, 1930, 183; W. Keil, *Z. physiol. Chem.*, 1930, **187**, 1; *A.*, 1930, 617.

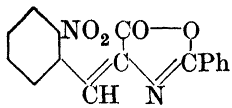
[66] W. Linneweh and F. Linneweh, *Z. physiol. Chem.*, 1930, **189**, 80; *A.*, 1930, 1049.

[67] K. S. Narang and J. N. Rây, *J.*, 1931, 976.

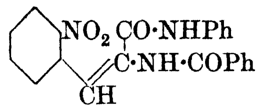
(IX). The latter gave 5-keto-1 : 2-diphenyl-4-*o*-nitrobenzylidene-4 : 5-dihydroglyoxaline (X) on treatment with phosphoryl chloride,



(VII.)



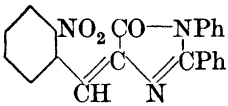
(VIII.)

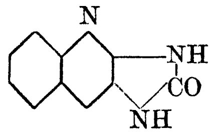


(IX.)

and the formation of the glyoxalinoquinoline (VII) was then effected by reduction with zinc dust and acetic acid. A related

(X.)



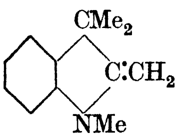


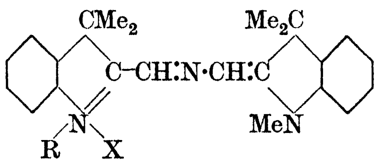
(XI.)

product (XI) has been obtained by the condensation of hydantoin with *o*-nitrobenzaldehyde, and the reduction of the 5-*o*-nitrobenzylidenehydantoin thus formed with hydriodic acid and phosphorus.[68]

Cyanine Dyes.—Of very considerable interest is the recent investigation [69] of the structure of indolenine-yellow, a dye obtained by the action of nitrous acid on 2-methylene-1 : 3 : 3-trimethylindoline (I) in acetic anhydride.[70] It was originally thought that the substance possessed the formula (II), but it has now been

(I.)

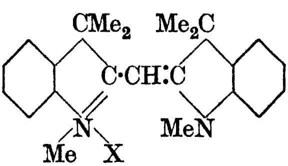


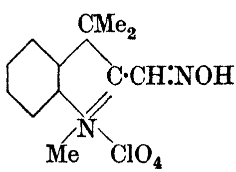


(II.)

shown that the reaction results in the elimination of hydrogen cyanide and that the constitution of the dye is, in reality, that of

(III.)





(IV.)

an indocyanine (III). The reaction is, therefore, very closely related to one already described [71] for the preparation of thiocyanines.

[68] J. Kozak and L. Musiał, *Bull. Acad. Polonaise*, 1930, [*A*], 432; *A.*, 366.

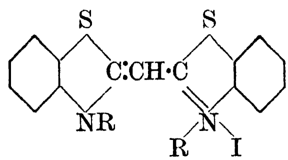
[69] R. Kuhn, A. Winterstein, and G. Balser, *Ber.*, 1930, **63**, [*B*], 3176; *A.*, 238.

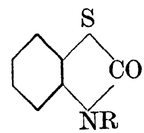
[70] D.R.-P. 459,616; *Chem. Zentr.*, 1928, i, 3119.

[71] Miss N. I. Fisher and Miss F. M. Hamer, *J.*, 1930, 2502; see *Ann. Reports*, 1930, **27**, 187.

When the methylene base (I) was treated in glacial acetic acid with sodium nitrite and then with perchloric acid, the perchlorate (IV) was isolated, and this was subsequently converted into indolenine-yellow (III) by heating with a further quantity of the base (I) in acetic anhydride. The latter stage involved the loss of water and hydrogen cyanide.

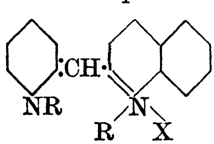
Another surprising new method for the production of thiocyanines (V) has been discovered;[72] it requires the interaction of methylmagnesium iodide and an *N*-alkylbenzthiazolone (VI) in benzene solution, and apparently involves the evolution of methane by a mechanism which is not at present obvious.

(V.)


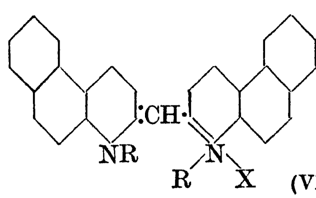


(VI.)

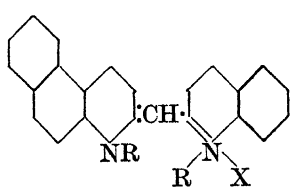
The scope of the *ψ*-cyanine reaction (the action of alkali on a mixture of the alkyliodides of 2-iodoquinoline and quinaldine), which has already been applied to the preparation of numerous types,[73] has now been further extended.[74] From 2-iodopyridine alkyliodide and quinaldine alkyliodide, the *ψ*-cyanines (VII) were obtained, while the analogous dyes (VIII) resulted from a similar reaction with 2-iodo-β-naphthaquinoline alkyliodide and β-naphthaquinaldine alkyliodide. The *ψ*-cyanines (IX) were prepared either from 2-iodoquinoline alkyliodide and β-naphthaquinaldine alkyl-



(VII.)



(VIII.)



(IX.)

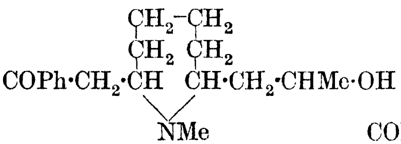
iodide or from quinaldine alkyliodide and 2-iodo-β-naphthaquinoline alkyliodide by the action of alkali. Analogous thio-*ψ*-cyanines were

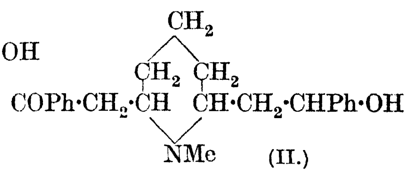
[72] W. König, W. Kleist, and J. Götze, *Ber.*, 1931, **64**, [*B*], 1664; *A.*, 1076.
[73] See *Ann. Reports*, 1928, **25**, 181; 1930, **27**, 186.
[74] Miss F. M. Hamer and Miss M. I. Kelly, *J.*, 1931, 777.

obtained by a similar process from 2-iodo-β-naphthaquinoline alkyliodide and 1-methylbenzthiazole alkyliodide.

Alkaloids.

Pyridine Group.—An extension of the recent work [75] on the nature of the products from *Lobelia inflata* has indicated the presence of several minor alkaloids, of which one—lobinine, $C_{18}H_{27}O_2N$—has been the subject of a detailed study.[76] The interesting conclusion is reached that this alkaloid may have the structure (I), in which there is a 7-membered ring. Its simple reactions clearly demonstrate its nature as an alcohol, a ketone, and a tertiary amine, and much of the evidence for the size of the ring system is derived from a study of the degradation of the corresponding diketone, $C_{18}H_{25}O_2N$. When the methiodide of the last substance was


(I.)

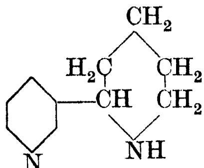

(II.)

treated with aqueous sodium bicarbonate, it gave dimethylamine and an unsaturated diketone, $C_{17}H_{20}O_2$, which was transformed ultimately into the corresponding saturated compound, $C_{17}H_{24}O_2$. The latter yielded, on oxidation, benzoic acid and suberic acid, $CO_2H{\cdot}[CH_2]_6{\cdot}CO_2H$, from which it is concluded that it has the formula $COPh{\cdot}[CH_2]_8{\cdot}COMe$. It is admitted, however, that these results could be accounted for on the basis of the structure $COPh{\cdot}[CH_2]_7{\cdot}CO{\cdot}CH_2Me$ for the saturated diketone, in which case it would be possible to formulate the alkaloid as a piperidine derivative similar to the better-known members of this group. Nevertheless, the 7-membered ring structure is favoured on the grounds that, unlike the other *Lobelia* alkaloids, lobinine gave neither 1-methylpiperidine-2 : 6-dicarboxylic acid nor 1-methyl-2-carboxypiperidine-6-acetic acid on oxidation. The relative positions of the carbonyl and hydroxyl groups are indicated by the fact that the alkaloid, like lobeline (II), readily yields acetophenone.

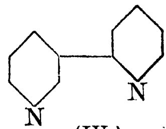
Preliminary work on the nature of the bases contained in *Anabasis aphylla* has been described,[77] and it is noteworthy that lupinine has been isolated from the lower-boiling fraction. In addition, a new alkaloid, anabasine, believed to be 3-(2′-piperidyl)pyridine (III) has

[75] See *Ann. Reports*, 1929, **26**, 169.
[76] H. Wieland, M. Ishimasa, and W. Koschara, *Annalen*, 1931, **491**, 14.
[77] A. Orechov and G. Menschikov, *Ber.*, 1931, **64**, [*B*], 266; *A.*, 498.

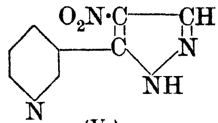
been obtained. In support of this structure it has been observed that the compound can be benzoylated and nitrosated. Oxidation with potassium permanganate gave nicotinic acid, and dehydrogenation resulted in the loss of six atoms of hydrogen and the formation of a product which is apparently 2 : 3′-dipyridyl (IV). The structure (III) has previously been advanced [78] for nicotimine,



(III.)



(IV.)



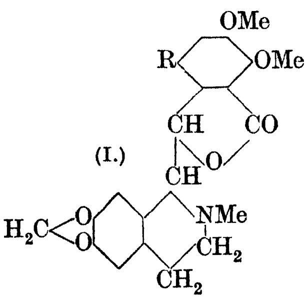
(V.)

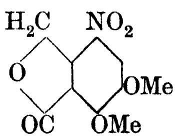
a minor alkaloid from tobacco, but the latter appears not to be identical with anabasine.

Of considerable interest is the observation [79] that a by-product, $C_8H_6O_2N_4$, always accompanies the nicotinic acid obtained by the oxidation of nicotine with nitric acid. The reactions of this compound suggest that it is 4-nitro-5-(3′-pyridyl)pyrazole (V), and its formation clearly involves very remarkable changes in the molecular structure.

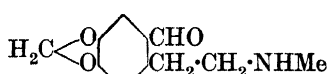
iso*Quinoline Group*.—A description has appeared [80] of the application to the synthesis of hydrastine (I; R = H) of two routes previously used [81] for the preparation of the closely related α-gnoscopine (*dl*-narcotine). The condensation of hydrastinine (II) and nitromeconine (III) led, on subsequent reduction, to a mixture of

(I.)





(III.)



(II.)

the two stereoisomeric, inactive aminohydrastines (I; R = NH_2). After separation of the mixture and removal of the amino-group *via* the hydrazino-compounds, the corresponding stereoisomeric

[78] A. Pictet, *Arch. Pharm.*, 1906, **244**, 388.

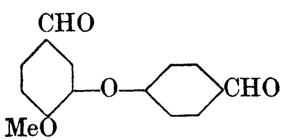
[79] G. A. C. Gough and H. King, *J.*, 1931, 2968.

[80] E. Hope, F. L. Pyman, F. G. P. Remfry, and R. Robinson, *J.*, 1931, 236.

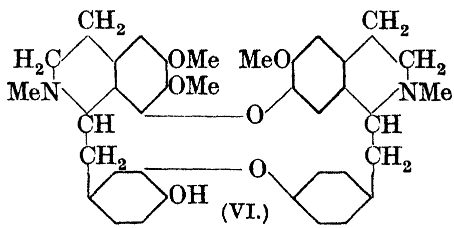
[81] E. Hope and R. Robinson, *J.*, 1914, **105**, 2086.

dl-hydrastines were obtained. Similarly, the condensation of hydrastinine with iodomeconine gave a mixture of the two stereoisomeric iodohydrastines (I; R = I). The exact relationship of these inactive forms to the natural *l*-hydrastine is not yet clear.

Earlier degradative experiments have indicated the main features in the constitution of oxyacanthine, and have enabled two formulæ, differing only in minor details, to be advanced for the alkaloid.[82] Further work [83] has now provided confirmation for these structural views. The product obtained from oxyacanthine methyl ether by the Hofmann degradation process gave two well-defined substances on oxidation with ozone. One of these proved to be 2′-methoxydiphenyl ether-4 : 5′-dialdehyde (IV) and yielded the corresponding dicarboxylic acid (already known) on further oxidation. The other was a base, $C_{25}H_{34}O_6N_2$, which contained three methoxyl groups and gave a dimethiodide. The latter salt was easily broken down by alkali to give trimethylamine and a nitrogen-free compound, $C_{21}H_{20}O_6$, which was found to be a dialdehyde containing two ethylenic linkages. These reactions are satisfactorily explained with the aid of formula (V) for the base $C_{25}H_{34}O_6N_2$, but there is no evidence yet to indicate the exact locations of the methoxyl groups and the ether linkage. Until such information is forthcoming, several alternatives of the type (VI) exist as possibilities for oxyacanthine. It is probable that one of these represents the closely related alkaloid berbamine.

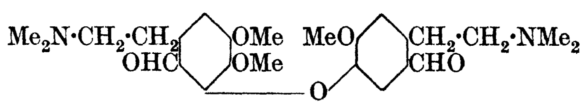


(IV.)



(VI.)

(V.)



In last year's Report [84] it was mentioned that the formula (VII) had been tentatively suggested [85] for chelidonine; valuable experimental evidence in support of this structure is now forthcoming.[86]

[82] *Ann. Reports*, 1929, **26**, 173.

[83] F. von Bruchhausen and P. H. Gericke, *Arch. Pharm.*, 1931, **269**, 115; *A.*, 636.

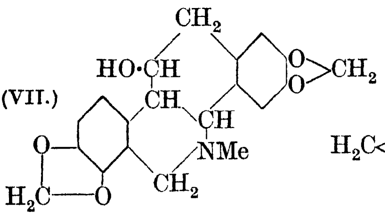
[84] *Ann. Reports*, 1930, **27**, 195.

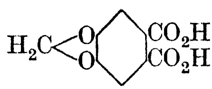
[85] F. von Bruchhausen and H. W. Bersch, *Ber.*, 1930, **63**, [*B*], 2520.

[86] E. Späth and F. Kuffner, *Ber.*, 1931, **64**, [*B*], 370; *A.*, 500.

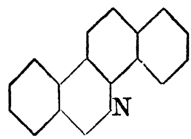
The oxidation of *N*-acetylanhydrochelidonine [87] with nitric acid has been found to yield benzene-1 : 2 : 4-tricarboxylic acid, while the oxidation of chelidonine with potassium permanganate gave hydrastic acid (VIII) and 3 : 4-methylenedioxybenzene-1 : 2-dicarboxylic acid. Confirmation of the nature of the fundamental ring systems in chelidonine and the closely related alkaloid sanguinarine is derived from the fact that the latter substance yields, on zinc dust distillation, a base which is now identified as α-naphthaphenanthridine (IX). The position of the alcoholic hydroxyl group is

(VII.)





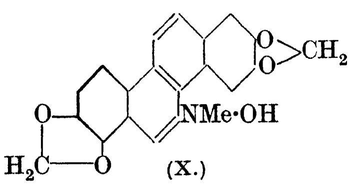
(VIII.)



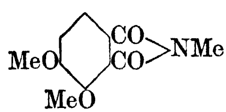
(IX.)

indicated by the results obtained from an application of the Hofmann and Emde degradation processes to chelidonine.

This structure for chelidonine being accepted, the known facts concerning sanguinarine and its relationship to the former alkaloid suggest for it the formula (X). The alkaloids homochelidonine, $C_{21}H_{23}O_5N$, and chelerythrine, $C_{21}H_{18}O_4N{\cdot}OH$, are very closely related to chelidonine and sanguinarine respectively, and probably differ from them only in having one of the two methylenedioxy-groups replaced by two methoxyl groups. On this assumption an investigation has been made [88] of some of the reactions of chel-



(X.)



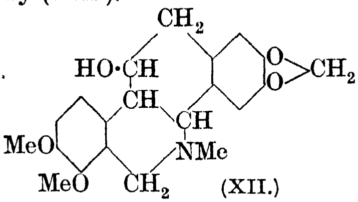
(XI.)

erythrine chloride in order to determine which methylenedioxy-group is involved. When oxidised with potassium permanganate under various conditions it yielded the methylimide (XI) of hemipinic acid and also hydrastic acid. It was observed, furthermore, that chelerythrine chloride gave α-naphthaphenanthridine (IX) on zinc dust distillation. The indications are, therefore, that homo-

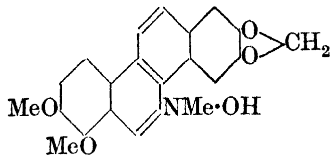
[87] Derived from chelidonine by acetylation as described by J. Gadamer, *Arch. Pharm.*, 1924, **262**, 265.

[88] E. Späth and F. Kuffner, *Ber.*, 1931, **64**, [*B*], 1123.

chelidonine is represented by the formula (XII) and chelerythrine by (XIII).

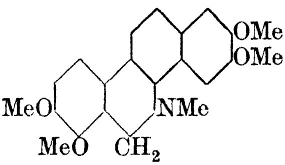


(XII.)

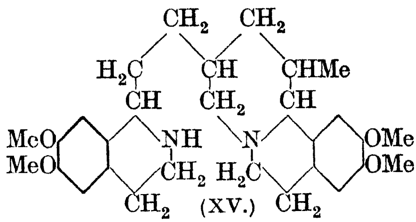


(XIII.)

The assumption regarding the nature of the relationship between chelerythrine and sanguinarine has been shown to be valid by removing the methylenedioxy-groups from dihydrochelerythrine and dihydrosanguinarine by treating these products with phloroglucinol and boiling 50% sulphuric acid. The hydroxy-compounds so obtained, on subsequent methylation, both yielded the same derivative [89] (XIV).

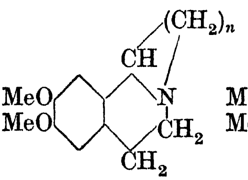


(XIV.)

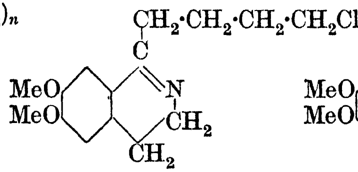


(XV.)

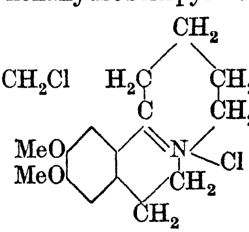
Reference has been made in a previous Report [90] to the preparation of substances which might, in view of the known facts concerning the structure of emetine, possess amœbicidal properties. Since it is thought that emetine can be represented by the formula (XV),[91] the work has now been extended [92] to the synthesis of the closely related 10 : 11-dimethoxy-1 : 2 : 3 : 4 : 6 : 7-hexahydrobenzpyrido-



(XVI.)



(XVII.)



(XVIII.)

coline (XVI; $n = 4$). This was accomplished by first converting δ-chlorovalero-β-veratrylethylamide,

$$CH_2Cl\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot C_6H_3(OMe)_2,$$

[89] E. Späth and F. Kuffner, *Ber.*, 1931, **64**, [*B*], 2034.

[90] *Ann. Reports*, 1929, **26**, 172.

[91] W. H. Brindley and F. L. Pyman, *J.*, 1927, 1067.

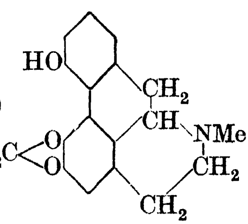
[92] R. Child and F. L. Pyman, *J.*, 1931, 36.

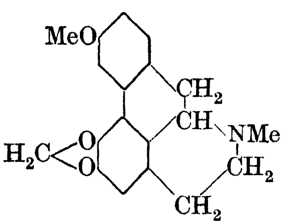
into 1-δ-chlorobutyl-6 : 7-dimethoxy-3 : 4-dihydro*iso*quinoline (XVII) by the action of phosphorus oxychloride. The latter gave the salt (XVIII) on warming, and the desired base (XVI; $n = 4$) was then obtained by reduction. A similar series of reactions starting from γ-bromobutyro-β-veratrylethylamide led to the analogous base (XVI; $n = 3$), but, when these products and some of the intermediates were examined, they were found not to possess pronounced physiological properties.

The view has been expressed [93] that trilobine and homotrilobine, alkaloids from species of *Cocculus*, belong to the 1-benzyltetrahydro-*iso*quinoline group, but the evidence so far available does not disclose the complete structures. The isolation of two additional alkaloids from *Cocculus trilobus* has also been described.[94] One of these, trilobamine, is apparently closely related to oxyacanthine and berbamine.

Aporphine Group.—It has been demonstrated [95] that three well-defined alkaloids of the aporphine type can be extracted from the bark of *Laurelia Novæ Zealandiæ*. One of these, pukateine (I), contains a methylenedioxy- and a phenolic hydroxyl group, and the formula assigned to it is based upon an examination of the products derived from an application of the Hofmann method of

(I.)

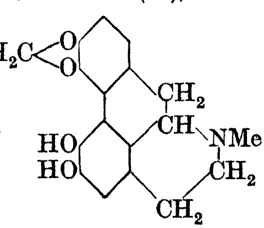


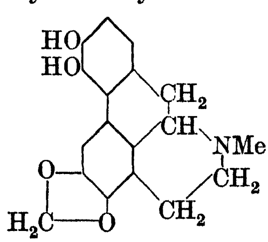


(II.)

degradation and from various processes of oxidation. The second alkaloid, laureline (II), contains a methylenedioxy- and a methoxy-

(III.)





(IV.)

group, but is different from pukateine methyl ether. Its degradative reactions support the formula (II). The third, laurepukine,

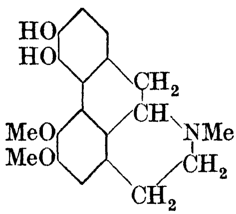
[93] H. Kondo and M. Tomita, *Chem. Zentr.*, 1931, i, 1114.

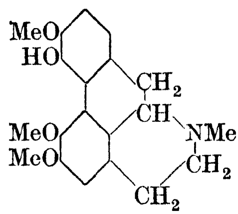
[94] H. Kondo and M. Tomita, *Arch. Pharm.*, 1931, **269**, 433.

[95] G. Barger and A. Girardet, *Helv. Chim. Acta*, 1931, **14**, 481, 504; *A.*, 749, 750.

which is now characterised for the first time, contains a methylenedioxy- and two phenolic hydroxyl groups. The evidence for its structure is less conclusive than in the two previous cases, but the alkaloid may be represented by the formula (III), or possibly (IV). Confirmation of these structural views from synthetical experiments will be awaited with interest.

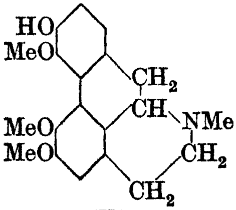
(V.)



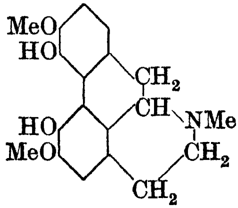


(VI.)

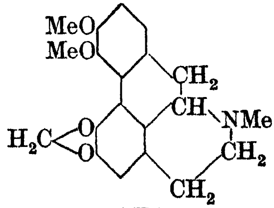
Considerable confusion has existed concerning the exact relative positions of the hydroxyl and methoxyl groups in certain well-known members of the aporphine class, although the locations of the oxygen atoms have been definitely established by the synthesis of the fully methylated derivatives. For some time past the formula (V) has been accepted for corytuberine, while the structures (VI) and (VII) respectively represent the prevailing views [96] regarding corydine and *iso*corydine (the two alternative monomethylcorytuberines). More recent work,[97] however, indicates the necessity for a further revision of these formulæ. Corytuberine diethyl ether, on oxidation with potassium permanganate, gave 4-methoxy-3-ethoxybenzene-1 : 2-dicarboxylic acid, a result incompatible with the structure (V). Furthermore, by partial ethylation of corytuberine, a mixture of the two possible monoethyl ethers was obtained, and this, on oxidation with potassium permanganate, gave the two products, 4-methoxy-3-ethoxybenzene-1 : 2-dicarboxylic acid and 5-methoxy-4-ethoxybenzene-1 : 2 : 3-tricarboxylic acid. It thus follows that corytuberine must be represented by the formula (VIII).



(VII.)



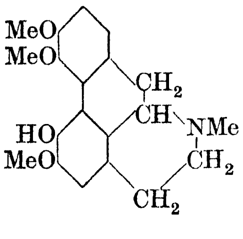
(VIII.)



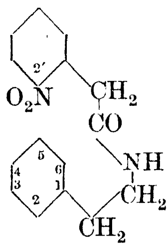
(IX.)

[96] J. Go, *Chem. Zentr.*, 1930, i, 234; *Ann. Reports*, 1930, **27**, 196.
[97] E. Späth and F. Berger, *Ber.*, 1931, **64**, [*B*], 2038.

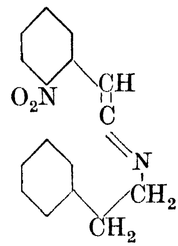
The structures of corydine and *iso*corydine were revealed in the following way. The methylenedioxy-group was removed from bulbocapnine methyl ether (IX) by treatment with phloroglucinol and sulphuric acid, and the resulting dihydric phenol gave corydine on partial methylation. Corydine must therefore have the structure (X), a fact which is confirmed by the observation that both corydine and its ethyl ether give 3 : 4-dimethoxybenzene-1 : 2-dicarboxylic acid on oxidation, and, in view of these results, the only possible formula for *iso*corydine is (VI).



(X.)



(XI.)



(XII.)

The earlier aporphine syntheses based on the Bischler–Napieralski reaction [98] have involved the formation of methyl ethers and so have thrown no light upon problems of the above type. The probability that synthetical methods may ultimately assist in settling some of these difficult points is now foreshadowed by a study [99] of the possibility of employing in these reactions materials in which phenolic hydroxyl groups are protected by carbethoxy or benzyl radicals. So far the experiments have not advanced beyond a preliminary exploratory stage, and further results will be awaited with interest.

Previous experience has shown [98] that the application of the Bischler–Napieralski reaction to the appropriate derivative of the amide (XI) proceeds satisfactorily only when a strongly *p*-directing group in the 3-position promotes the formation of the *iso*quinoline ring. In other cases the main reaction results in an alternative dehydration process with the production of neutral substances to which the structure (XII) has been assigned. A further study of the conditions which promote or prevent the formation of an *iso*quinoline derivative in such cases has recently been made,[1] and it is clear that the effect of the 2′-nitro-group on the neighbouring methylene group is such as greatly to assist the alternative process, since it has been found that 4′-methoxyphenylaceto-β-phenylethylamide (XIII) readily yields 1-*p*-methoxybenzyl-3 : 4-dihydro*iso*-

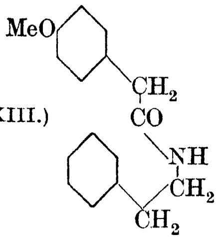
[98] See *Ann. Reports*, 1928, **25**, 185; 1929, **26**, 174.

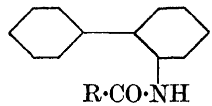
[99] J. M. Gulland and his collaborators, *J.*, 1931, 2872, 2881, 2885, 2893.

[1] H. Kondo and S. Ishiwata, *Ber.*, 1931, **64**, [*B*], 1533.

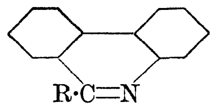
quinoline when treated with phosphorus oxychloride in boiling toluene. The 2′-nitro-group is, however, necessary for the completion of the aporphine synthesis, and its effect is overcome only when such groups as methoxy and benzyloxy are present in the 3-position.

(XIII.)





(XIV.)

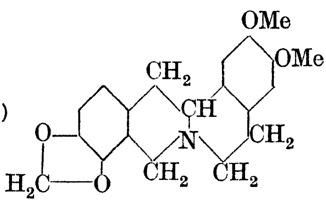


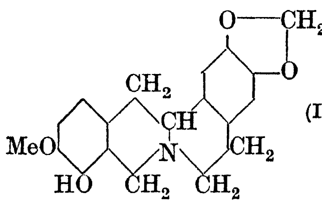
(XV.)

Another interesting application of the Bischler–Napieralski reaction is observed in the facile conversion of numerous acyl-*o*-xenylamines (XIV) into the corresponding phenanthridine derivatives (XV) by heating with phosphorus oxychloride.[2]

Diisoquinoline Group.—Further confirmation of the fact that sinactine, an alkaloid from *Sinomenium acutum*, must be regarded as *l*-tetrahydro*epi*berberine (I) has been obtained by the resolution of a synthetical specimen of *dl*-tetrahydro*epi*berberine.[3] The properties of the *l*-form of the latter base were found to be in agreement with those described for the natural product.

(I.)





(II.)

Some time ago evidence was produced[4] to show that nandinine, an alkaloid from *Nandina domestica*, is *d*-tetrahydroberberrubine (II), but considerable doubt is now cast upon its real nature as the result of a recent investigation[5] of the purification and resolution of tetrahydroberberrubine. It is found that the physical constants of *d*-tetrahydroberberrubine are in reality quite different from those given for nandinine.

Lupin Alkaloids.—The past year has been one of great activity in the field of the chemistry of the lupin alkaloids. Some of the

[2] G. T. Morgan and L. P. Walls, *J.*, 1931, 2447.

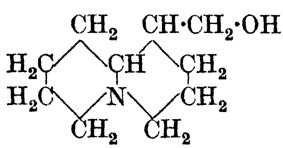
[3] E. Späth and E. Mosettig, *Ber.*, 1931, **64**, [*B*], 2048.

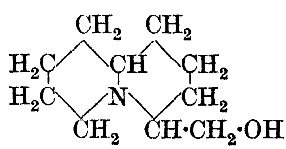
[4] Z. Kitasato, *Acta Phytochim.*, 1927, **3**, 175; *Ann. Reports*, 1927, **24**, 172.

[5] E. Späth and W. Leithe, *Ber.*, 1930, **63**, [*B*], 3007; *A.*, 242.

published statements are polemical in character, so that much confusion exists, but, since most of the work has been directed towards testing recent structural formulæ, the results are of considerable general interest.

Although the homogeneity of lupinine has been doubted during the year, it now seems certain that the substance which melts at 68—69° is a single compound.[6] Interesting results, however, have been obtained [7] from the degradation of a less pure specimen (m. p. 63—65°) derived from the seeds of the yellow lupin, and it is claimed that these support Karrer's formula (I) for the alkaloid. For instance, lupinane, $C_{10}H_{19}N$, obtained by the dehydration and subsequent hydrogenation of the alkaloid, was converted into bromolupinanecyanoamide, $C_{11}H_{19}N_2Br$, on treatment with cyanogen bromide. The lupinanecyanoamide, $C_{11}H_{20}N_2$, obtained from the latter by removal of the bromine, yielded a secondary piperidine base, $C_{10}H_{21}N$, on hydrolysis. Dehydrogenation of the latter with silver acetate in acetic acid at 180° led to the corresponding tertiary pyridine base, $C_{10}H_{15}N$, which was shown by oxidation to be a mixture of 3-methyl- and 6-methyl-2-*n*-butylpyridine. Thus, by the action of potassium permanganate, the following products were obtained: 2-*n*-butylpyridine-6-carboxylic acid, 2-methylpyridine-6-carboxylic acid, pyridine-2 : 3-dicarboxylic acid, and 3-methylpyridine-2-carboxylic acid. These results can be explained with the aid of Karrer's formula, but require the assumption that the lupinine used contained an isomeride (II), to which the name "*allo*lupinine" has been assigned; the relative amounts of the oxidation products indicated that the base (I) preponderated. It has been more recently stated [8] that the pyridine derivatives which suggest the presence of *allo*lupinine are not obtained from a specimen of lupinine melting at 68—69°.

(I.) 

 (II.)

Of considerable importance in connexion with the structure to be assigned to lupinine is the recent synthesis [9] of octahydropyridocoline (III). This has been achieved by first condensing ethyl piperidine-2-carboxylate with γ-bromobutyronitrile to give the

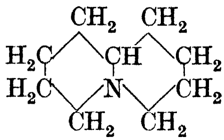
[6] C. Schöpf, E. Schmidt, and W. Braun, *Ber.*, 1931, **64**, [*B*], 683; *A.*, 635; P. Karrer, *ibid.*, p. 942; *A.*, 750.

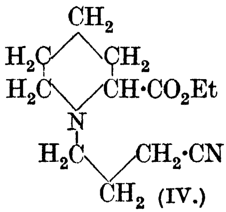
[7] K. Winterfeld and F. W. Holschneider, *ibid.*, p. 137; *A.*, 370.

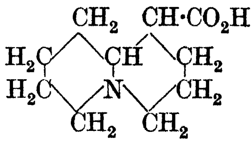
[8] K. Winterfeld, *ibid.*, p. 692; *A.*, 635.

[9] G. R. Clemo and G. R. Ramage, *J.*, 1931, 437.

nitrile (IV). The corresponding dicarboxylic ester, prepared from this by the action of alcoholic hydrogen chloride, was submitted to the Dieckmann reaction, and ethyl 1-keto-octahydropyridocoline-


(III.)


(IV.)


(V.)

2-carboxylate was obtained. 1-Keto-octahydropyridocoline, prepared from the latter by hydrolysis with dilute sulphuric acid, yielded octahydropyridocoline when reduced with amalgamated zinc and concentrated hydrochloric acid.

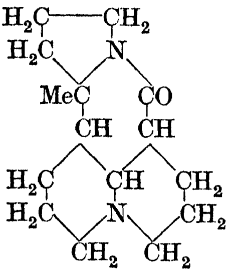
Although the decarboxylation of lupininic acid (V) with soda-lime leads to a complex mixture, there has been isolated from it, after reduction with palladium and hydrogen, a base, $C_9H_{17}N$, which has the same molecular formula as, but is not identical with, octahydropyridocoline. This result does not of necessity invalidate Karrer's formula for lupinine, since fundamental changes of structure may occur during the formation of the new base.

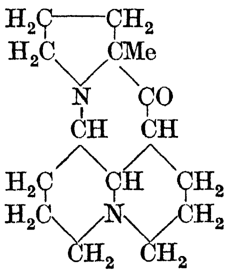
The fact that lupanine, $C_{15}H_{24}ON_2$, and sparteine, $C_{15}H_{26}N_2$, are structurally closely related is made probable by the interesting observation [10] that *d*-lupanine can be reduced with hydriodic acid and red phosphorus to a base which appears to be identical with natural *l*-sparteine. In an attempt to establish one of the four alternative formulæ previously advanced by Karrer and his collaborators [11] for sparteine, the alkaloid has now been degraded to a saturated hydrocarbon, $C_{15}H_{32}$, by repeated applications of the Hofmann process and catalytic hydrogenation of the intermediate products.[12] On the basis of these four formulæ this hydrocarbon might be one of three isomeric pentadecanes, all of which have been prepared synthetically, but the physical properties are such as to lead to no really definite conclusions.

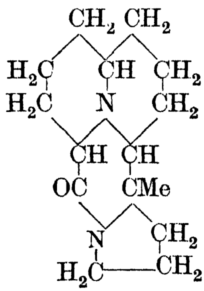
Interesting alternative views concerning the structures of lupanine and sparteine have been advanced. It has been reported that lupanine has now been made to yield β-lupinane, $C_{10}H_{19}N$, and an oily product which gives the pyrrole pine-shaving reaction, by heating with fuming hydriodic acid and red phosphorus for fifty

[10] G. R. Clemo, R. Raper, and C. R. S. Tenniswood, *J.*, 1931, 429.
[11] See *Ann. Reports*, 1929, **26**, 182.
[12] P. Karrer, B. Shibita, A. Wettstein, and L. Jacubowicz, *Helv. Chim. Acta*, 1930, **13**, 1292; *A.*, 241.

hours at 240°. In view of this result and the fact that sparteine can be degraded to 2-methylpyrrolidine, the formula (VI), or some closely related alternative such as (VII), may represent lupanine.[13] The sparteine structure is derived by replacing the >CO group by $>CH_2$. Hydroxylupanine, $C_{15}H_{24}O_2N_2$, would have the same fundamental structure, differing from lupanine in having a hydroxyl group in the place of a hydrogen atom. Lupanidine, which has been isolated [14] from the mother-liquors of lupinine and is isomeric with lupanine, may have the structure (VIII) in view of the possible presence of *allo*lupinine in crude lupinine. These views must at present be regarded as rather speculative. In fact, the soundness of the experimental work upon which they are partly based has been questioned.[15] Thus it has been asserted that β-lupinane cannot be obtained from pure lupanine by the action of hydriodic acid and red phosphorus, and that its isolation in the work described above may be explained by the presence of lupinine in the sample


(VI.)


(VII.)

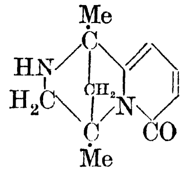
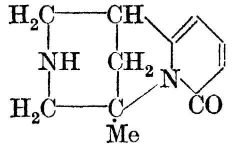

(VIII.)

of lupanine employed. This criticism has, however, been resisted,[16] and it has been re-affirmed that β-lupinane can be obtained from lupanine.

Cytisine, an alkaloid from the seeds of *Cytisus laburnum*, may ultimately prove to be closely related to the lupin bases. Although comparatively little evidence is at present available regarding its constitution, the few known reactions of the substance are not all satisfactorily explained by the formulæ hitherto put forward, and some recent structural views [17] are accordingly of interest. The alternative formulæ (IX) and (X) have been suggested partly as the result of an examination of the products of the exhaustive methylation of the alkaloid. If these views are sound, the pro-

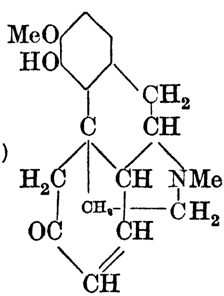
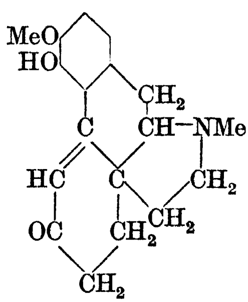
[13] K. Winterfeld and A. Kneuer, *Ber.*, 1931, **64**, [*B*], 150; *A.*, 371.
[14] A. Kneuer, Diss., Freiburg i. Br., 1929.
[15] G. R. Clemo, Miss G. C. Leitch, and R. Raper, *Ber.*, 1931, **64**, [*B*], 1520.
[16] K. Winterfeld, A. Kneuer, and F. W. Holschneider, *ibid.*, p. 2415.
[17] H. R. Ing, *J.*, 1931, 2195.

duction of 6 : 8-dimethylquinoline, 2-hydroxy-6 : 8-dimethylquinoline, and ammonia when cytisine is reduced with hydriodic acid and

(IX.)   (X.)

red phosphorus must involve primarily a rupture of the pyrrocoline skeleton, followed by the formation of the quinoline nucleus. Other reactions of the alkaloid can be accounted for with the aid of these formulæ, but the direct evidence for the pyrrocoline structure is at present scanty.

Morphine Group.—The production of thebainone (I) during the complex transformations of the morphine alkaloids has not hitherto been observed,[18] although some simple derivatives of it have been isolated. It has now been reported,[19] however, that it accompanies metathebainone (II) in the product of the reduction of thebaine by means of stannous chloride and concentrated hydro-

(I.)   (II.)

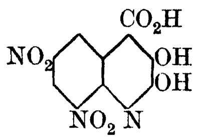
chloric acid, and, under the most favourable conditions, may form the main constituent. It is also produced during the reduction of codeinone under similar conditions. These results have enabled interesting deductions to be made concerning the complex changes which ensue when thebaine is treated with concentrated hydrochloric acid, but the latter cannot be adequately dealt with in the scope of this Report.

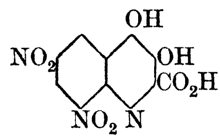
Strychnine.—Although much published work dealing with strychnine and brucine has again appeared during the year, the

[18] The "thebainone" prepared by Pschorr by reducing thebaine with stannous chloride and concentrated hydrochloric acid is now called "metathebainone" in accordance with the revised nomenclature of this group (see *Ann. Reports*, 1930, **27**, 197).

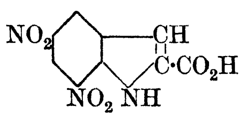
[19] C. Schöpf and H. Hirsch, *Annalen*, 1931, **489**, 224.

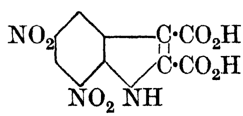
chemistry of this group is so complex that only that which has a very direct bearing on suggested structural formulæ can excite widespread interest, and only those aspects will be surveyed in this review. In the development of the recent formulæ for strychnine [20] much has depended upon the nature of dinitrostrycholcarboxylic acid. Last year, from the evidence then available, this acid was regarded [21] as possessing one of the formulæ (I) and (II). Subsequent investigations [22] have shown, however, that dinitrostrychol can be transformed by the usual Curtius reactions into a urethane, so that it must now be considered not as a dihydroxy-

(I.) 

 (II.)

quinoline but as an indolecarboxylic acid, probably of the structure (III). Dinitrostrycholcarboxylic acid, therefore, is 5 : 7-dinitroindole-2 : 3-dicarboxylic acid (IV). The stability of dinitrostrychol is very surprising and is largely responsible for the failure to recognise its true nature at an earlier date. The latest strychnine

(III.) 

 (IV.)

formula, containing a quinoline skeleton, now rests on a less solid foundation, but it is not necessarily definitely excluded by this recent development. It is important to observe, however, that the doubt which has existed regarding the presence of the quinoline system in dinitrostrycholcarboxylic acid has been coupled with the opinion [23] that the strychnine molecule contains a dihydroindole skeleton, which was a feature of the earlier formula of Fawcett, Perkin, and Robinson.

Of some interest is the isolation [24] of three new alkaloids from the strychnine mother-liquors. These are α-colubrine, $C_{22}H_{24}O_3N_2$, the isomeric β-colubrine, and ψ-strychnine, probably $C_{21}H_{22}O_3N_2$ or $C_{21}H_{24}O_3N_2$.

S. G. P. PLANT.

[20] See *Ann. Reports*, 1928, **25**, 193; 1929, **26**, 181; 1930, **27**, 199.
[21] K. N. Menon, W. H. Perkin, and R. Robinson, *J.*, 1930, 830.
[22] K. N. Menon and R. Robinson, *J.*, 1931, 773.
[23] H. Leuchs, *Ber.*, 1931, **64**, [*B*], 461.
[24] K. Warnat, *Helv. Chim. Acta*, 1931, **14**, 997; *A.*, 1312.

ANALYTICAL CHEMISTRY.

One of the most interesting analytical publications of the year is the "Festschrift" to Wilhelm Böttger [1] contributed by his pupils and co-workers. This contains an important paper by I. M. Kolthoff embodying a fundamental discussion of the sensitiveness of precipitation reactions,[2] which sets out from the rule laid down by Böttger many years ago, namely, $E = L + S$, where E is the sensitiveness, L is the solubility on the Nernst solubility law, and S is the visibility of the precipitate. This rule held strictly for silver halides, but failed in other cases, since the expression involved the assumption that L and S were constant. Such an assumption could scarcely hold strictly except in the few cases of precipitates where the solubility and visibility are largely independent of the particle size and method of precipitation. Now the variation of solubility with particle size for a completely dissociated salt of low solubility may be derived by means of the expression $RT/M \,.\, \log S_r/S = 2\sigma/\rho r$, in which S_r/S is the ratio of the solubility of particles of small radius r (of the order of $<\mu$) to that of the solubility of fair-sized crystals, ρ is the density, and σ the surface tension, other letters bearing their usual meaning. If the value of S_r/S is calculated for various insoluble substances, *e.g.*, barium sulphate or silver chloride, it is found that increases of solubility of altogether different orders of magnitude are found, quite apart from questions of the crystalline or colloidal character of the precipitates. This consideration goes a long way towards explaining the differences found in the quantitative precipitation of substances of the same order of solubility. It also points to the necessity for careful specification of the size of the precipitated particles when "supersaturation" is considered in relation to quantitative precipitation, for the solubility of barium sulphate, for example, may be nearly 1000 times as great for small as for large crystals of the order of 2μ, whereas that of silver chloride remains almost constant within a much wider range of particle size. It follows, further, that if the first precipitate of barium sulphate from a very dilute sulphate solution is very small, the solution is not saturated with reference to barium sulphate. On this account, as well as that of size of precipitated particle, and departure from Rayleigh's law of scattering of light, the visibility term S of Böttger's expression cannot be regarded as constant even for the same sub-

[1] *Z. anal. Chem.*, 1931, **86**, 1—190. [2] *Ibid.*, p. 34.

stance. Now the intensity of light scattered by particles of small dimensions varies as nv^2/λ^4, where n is the number of scattering particles, v the volume of the particles assumed to be of equal size, and λ is the wave-length of the scattered light. Where the particles are less than 0·1 μ the law is valid. If it is applied to a fixed quantity of precipitate, the peculiar result emerges that the brightness of the scattered light may be much less although the number of scattering particles is increased enormously. For example, if the particles are 0·01 μ at the start, and grow to 0·1 μ on standing, the intensity of the light scattered in the first case is far less than that of the second case of the larger particles, despite the fact that originally there were 1000 times as many scattering particles. This consideration emphasises once again the necessity for the strictest regulation of the conditions of precipitation in nephelometric measurements in order to obtain particles of constant size with which to conduct determinations. It also indicates the need for the observer to obtain calibration curves for each substance he is estimating. When nephelometric determinations of sols are made, this is still more necesary, since the intensity of the scattered light does not then follow the law in all cases.[3]

The desirability of careful reconsideration of each case where nephelometric methods are to be employed in atomic-weight determinations and similarly accurate work is discussed by C. R. Johnson in a series of papers.[4] It is commonly assumed that the equal opalescence end-point as used by Richards and Wells for the sodium chloride–silver titration is equally applicable in all cases. Now, the nephelometric method is remarkably sensitive, quite small changes in the character of the sols causing relatively large variations in intensity of the scattered light. Hence the assumption that the opalescence end-point will be equally balanced for multivalent as for univalent ions does not necessarily apply. In fact, if the vastly different coagulating powers of multivalent and univalent ions are taken into consideration, it seems more probable that the former ions will favour unbalanced actions, thus rendering the equal-opalescence end-point method doubtful until it has been shown definitely to apply to any particular multivalent ion. Johnson therefore suggests an alternative end-point, called "standard solution end-point," the object being to determine the absolute quantities of silver and halide ions in the liquid under the conditions of the test, rather than the relative quantities as is usually the case. It is shown that shaking and cooling of the supernatant liquid in determining the

[3] H. Bechold and F. Hebler, *Kolloid-Z.*, 1922, **31**, 70.

[4] *J. Physical Chem.*, 1931, **35**, 540, 830, 2237, 2581; *A.*, 456, 584, 1141, 1256.

quantity of chloride may result in leaving an excess of halide in the supernatant liquor, and such a result would have the effect of lowering the value for the calculated atomic weight.

The magneto-optic method of analysis has been applied to the investigation of the isotopes of Au, Pt, Rh, Ru, Ta, and Th,[5] but the search for element 87 by the method indicated that there is a possibility of obtaining values for the time-lags between Faraday effect and magnetic field, which are the same for different complex ions of very nearly equal molecular weights. Thus, complex ions such as $SnCl_3^{\cdot}$ or $ReCl^{\cdot}$ will have a molecular weight of about the same magnitude as would be expected for the atomic weight of element 87 and would thus appear in the same position when investigated by magneto-optic analysis.

For some time past, investigations of spectral absorption of high precision have been carried out in the infra-red region of the spectrum, mostly by means of apparatus depending upon the effect of the infra-red radiation transmitted by gases or liquids, on thermopiles of great delicacy, combined with galvanometers of high sensitivity. The technique is not easy, but the circumstance that certain groups of atoms gave characteristic bands in the infra-red pointed to the possibility of utilising the measurement of these bands as a means of analysis. It is, for example, now well established that compounds with a C–H group always show oscillation bands very close to 0·9 μ, 1 μ, and 3·4 μ, a fact which is easily seen when the bands of chloroform and carbon tetrachloride are compared. The introduction of "neocyanine" sensitised photographic plates permits of the photography of the near infra-red up to about 1 μ and beyond with some ease and rapidity, and it therefore becomes possible to utilise glass spectrographs in this region. In this way, it has been found possible to detect 1% of ethyl or butyl alcohol in carbon tetrachloride, for these substances show the characteristic bands of C–H, but also show the –OH oscillation band at 0·96 μ. This band does not disappear until the concentration of the alcohol is lower than 0·1%.[6] It is an interesting point, theoretically, to observe that the 0·96 μ band has its maximum at about 20% concentration of the alcohol and it becomes weaker on dilution. This peculiarity is similar to that observed in the Raman effect with nitric acid, which was attributed to electrolytic dissociation, and a similar explanation is advanced to explain the diminution in intensity of the –OH bands of the alcohol when dissolved in carbon tetrachloride.

Owing to the comparative ease with which the Raman spectra

[5] F. Allison and E. J. Murphy, *Physical Rev.*, 1930, [ii], **36**, 1097.

[6] R. Freymann, *Compt. rend.*, 1931, **193**, 928.

may be obtained, it is not surprising that the attempt to bring the method into use as an analytical procedure is receiving attention. It is found that α- and β-pinene, carene, and camphene show characteristic displacements of the scattered radiation, and that a terpene mixture gives the Raman spectra of all the constituents. Since these spectra are readily picked out, the possibility arises of utilising the effect quantitatively.[7] A further application is in the detection of isomerides. For instance, Δ^{α}-hexene in methylethyl*cyclo*propane gives its characteristic Raman line, 1642 cm.$^{-1}$, so that some 2% of the hexene is detectable.[8]

The use of arc and spark spectra in the quantitative determination of metals in alloys has made important advances in convenience of application and certainty of results. Particularly striking are the results now obtained [9] by utilising for the photometer the rotating logarithmic wedge-sector as applied originally to spectrum analysis by Scheibe and Neuhäusser. The rotating sector in this case is of entirely different character from that usually employed in determining extinction coefficients in absorption spectra. It consists of a disc from which a part of the periphery is cut away in such a manner that the circumferential aperture, θ (expressed as a fraction of one complete revolution), measured at a distance l radially inwards from the outermost part of the disc, follows the relation $-\log\theta = 0{\cdot}3 + 0{\cdot}2\,l$. The advantage of this scheme is that small variations in the arc or sparking voltages, or in the development of the photographic plates, do not throw the results out. This was one of the defects of the earlier methods employed by Hartley, Pollock, de Gramont, and others. From the shape of the sector opening in front of the spectrograph slit, it follows that the spectrum lines are thin wedges instead of the ordinary parallel-sided lines. The length of the wedges varies with the intensity of the lines, this being the effect of cutting the sector to accord with the logarithmic expression given above. In order, then, to apply the method in practice to a metal, say nickel in steel, a number of spectra of standard specimens of nickel steel is photographed, and the difference in the length of the wedge given by some well-known nickel line from that of a neighbouring iron line is plotted against the percentage of nickel. It will be seen that, by employing this difference method of " line-pairs," small variations in conditions are eliminated since it is known experimentally that the differences remain constant. In a typical case,

[7] G. Dupont, P. Daure, and J. Allard, *Bull. Soc. chim.*, 1931, [iv], **49**, 1401.

[8] R. Lespieau, M. Bourguel, and R. L. Wakeman, *Compt. rend.*, 1931, **193**, 238; *A.*, 1147.

[9] F. Twyman and C. S. Hitchen, *Proc. Roy. Soc.*, 1931, [*A*], **133**, 72; *A.*, 1260.

for example, the arc lines Ni λ 3415 and Fe λ 3418 are employed, permitting reasonably accurate and rapid determinations of nickel in steel to be made up to 5% of the element.[10] A further advantage of the wedge-sector method is that it has been successfully employed for determining metals in their solutions as chlorides. In this case, a special kind of sparking vessel for the solutions was devised, ensuring constant supply of fresh liquid during the time required for photographing the spectrum, and eliminating difficulties arising from decomposition of the solutions around the electrodes and from incrustations. For solutions, an " internal standard " is obtained by adding a known and definite amount of the chloride of some metal which does not occur as an impurity in the material under examination, but which gives lines close to those of the metal being determined. It is often possible to choose pairs of lines, one from the standard and one from the metal, whose relative intensities are not affected by varying spark conditions, so-called " homologous pairs " of lines.[11] The extent to which spectrum analysis has now been carried is well illustrated by its utilisation for the analysis of minerals.[12] While it is too much to expect that a complete analysis of a mineral can be made in this way, it is undoubtedly the fact that many of the metallic elements and some of the non-metals can be determined very accurately by spectroscopic methods. The sensitiveness of the method may be very great indeed. It has been shown that as little as 1 γ of chromium can be detected with a carbon arc, and as small a quantity as $6 \times 10^{-2}\,\gamma$ when dissolved in fused alumina.[13] Again, as little as 0·5 part per million of aluminium can be estimated approximately in the ashes from biological material,[14] using pure copper electrodes for production of the arcs. A comprehensive investigation on the determination of certain elements such as titanium in aluminium by utilisation of " homologous pairs of lines " is now available, with details of the manner in which this procedure may be utilised practically.[15]

Attention is directed to a development in the methods of determining halogens, including fluoride, in organic compounds. There are few convenient and rapid methods for this purpose, especially in compounds containing high proportions of halogens. The process employing sodium and absolute alcohol fails in many cases, giving low results, and the method of oxidation by hot sulphuric acid and

[10] F. Twyman and A. A. Fitch, *J. Iron Steel Inst.*, 1930, ii, 289.

[11] E. Schweitzer, *Z. anorg. Chem.*, 1927, **164**, 127.

[12] See F. Löwe, *Fortschr. Min.*, 1927, **12**, 220.

[13] J. Papish and W. J. O'Leary, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 11; *A.*, 455.

[14] D. Tourtelotte and O. S. Rask; *ibid.*, p. 97; *A.*, 662.

[15] A. Schleicher and J. Clermont, *Z. anal. Chem.*, 1931, **86**, 191, 271.

an oxidising agent also has limitations and requires special apparatus for successful operation. E. Chablay [16] first utilised the action of sodium dissolved in liquid ammonia for determining halogens in organic compounds, and this was followed by F. B. Dains and his co-workers [17] and by C. W. Clifford.[18] The process has been re-examined and simplified so that it is available as an ordinary laboratory method. In some cases, where two halogen atoms are attached to the same carbon atom, cyanide is formed, but this is eliminated in the process described by T. H. Vaughn and J. A. Nieuwland.[19] To avoid the delay in decomposition resulting from insolubility of the organic compound in liquid ammonia, an organic liquid unacted on by sodium in ammonia is added, *e.g.*, dimethylacetal or ether. The reaction is then complete in a few minutes, and ammonium nitrate is added to the liquid ammonia before this is allowed to evaporate and the excess of sodium destroyed. The halogen is determined in the sodium halide by the usual methods, and the process is stated to be suitable for micro-determinations. An important advantage of this method is that it can be used to decompose organic fluorine compounds containing other halogens as well.

Some definite advances are announced in the practical development of the use of thermionic valves as accessories for determining p_H values and in potentiometric titrations of all kinds. Especially important is the use of non-aqueous solvents as applied to the determination of the acidity of organic substances such as oils. One of the earlier suggestions was to use amyl or (later) butyl alcohol saturated with lithium chloride and containing quinhydrone.[20] At first, the alcoholic solution of lithium chloride was used both as a reference half-cell and for dissolving the oil, but later a silver–silver chloride half-cell was found to answer. Since a saturated solution of lithium chloride in butyl alcohol is not a good solvent for oils or resins, a more convenient method was devised by B. L. Clarke, L. A. Wooten, and K. G. Compton.[21] In this case the problem is to overcome the difficulty arising from butyl-alcoholic solutions of high specific resistance. The principle adopted for measuring the titration is to arrange the circuit so that any change in the potential of the indicator electrode causes a large deflexion of some indicating meter, and this is secured by using vacuum tubes which have high grid insulation. The procedure is to dissolve the oil in dry butyl alcohol containing a little quinhydrone, and add about one-tenth of

[16] *Ann. Chim.*, 1914, [ix], **1**, 510.
[17] *J. Amer. Chem. Soc.*, 1918, **40**, 936; 1920, **42**, 1573.
[18] *Ibid.*, 1919, **41**, 1051.
[19] *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 274; *A.*, 1393.
[20] H. Seltz and L. Silverman, *ibid.*, 1930, **2**, 1; *B.*, 1930, 248.
[21] *Ibid.*, 1931, **3**, 321.

the volume of saturated lithium chloride–butyl alcohol mixture. The liquid is kept free from air in a flask filled with nitrogen, and the indicator electrode is bright platinum wire immersed in the liquid, the reference electrode being a calomel half-cell with an agar-agar salt bridge. A curve is plotted for the titration, giving micro-ammeter deflexions against volume of reagent used. Very sharp maxima of the curves are readily obtained at the end-point.

The problem of potentiometric titrations in cases where readily reducible substances are present and the hydrogen electrode is inapplicable is one that arises from time to time in practice. Tungsten electrodes seemed to present possibilities and were found to be useful in certain solutions;[22] they would appear to offer scope for more extended application. A useful electrode is the antimony–antimonous oxide electrode, for it has been shown to be available for such difficult titrations as hydrocyanic, sulphurous, selenious, and telluric acids with a very fair degree of accuracy.[23]

Despite its convenience, the glass electrode has not received the extended use it deserves in determinations of p_H values, although it can be used for measurements up to p_H 9·5 or thereabouts. Part of this is doubtless due to the very high resistance of the glass bulbs used, but this need not be serious if the special glass now available is used, for the resistance may be reduced to a few megohms, thereby permitting the convenient utilisation of the valve electrometer. An important scheme is given in detail by C. Morton [24] for the determination of glass-electrode potentials by a ballistic method which gets rid of a troublesome feature, namely, the "creeping" of the zero of the galvanometers. This has been accomplished by the introduction into the anode circuit of a high resistance, across which is the galvanometer in series with a large capacity of 4 μF or so. We have found this scheme quite satisfactory in use, especially where observations have to be continued over long periods.

There is not much information available on p_H values at comparatively high temperatures, despite the necessity for having such data when determinations have to be made in conditions where cooling is inadvisable. The scheme laid down by S. Stone [25] is therefore of importance. It describes suitable forms of electrode vessels and electrodes. The silver–silver chloride reference electrode is used in conjunction with a platinum–hydrogen electrode, and p_H values for buffer mixtures up to 10 and above 100° are recorded. The change in p_H may be positive or negative and is nearly constant in most mixtures for a considerable range of p_H.

[22] H. T. S. Britton and E. N. Dodd, *J.*, 1931, 829; *A.*, 699.
[23] H. T. S. Britton and R. A. Robinson, *ibid.*, p. 458; *A.*, 585.
[24] *Ibid.*, p. 2977. [25] *Rec. trav. chim.*, 1930, **49**, 1133; *A.*, 184.

There is little doubt that, wherever possible, actual determination of the p_H by a potentiometric method is on the whole more satisfactory than colorimetric methods, which are, however, good enough for much practical work when it is sufficient to know the p_H within about $\pm$ 0·1 unit. Numerous factors influence the accuracy of the colorimetric tests, such as salt effects, protein effects, and particular errors due to the indicators themselves. Wide-range indicators have to be used with care and may lead to erroneous results in unbuffered solutions such as extracts obtained in paper testing, from soils, sugar liquors, and so on. These indicators are safe with well-buffered liquids or in those cases where the p_H of the indicator is near that of the liquid under test. It is usually better to use a number of short-range indicators whenever the solution is suspected to be unbuffered.[26] A further consideration in the preparation of the indicators is that considerable variations in colour may occur in several ways, especially from the method of preparing the indicator, its storage, and purity.[27]

It must always be remembered in the use of coloured indicators for determining p_H, that salts may have a definite effect on the colour of an indicator, and that this varies with the concentration of the latter. This effect has been measured and even applied to determine the dissociation of acetic acid.[28] The salt error may with some indicators be serious enough in certain alkaline buffers themselves, *e.g.*, glycine buffers, to show large discrepancies between the p_H values of sodium hydroxide solutions and those of the standard buffer which gives the same colour with the indicator.[29] These considerations emphasise the necessity for considering carefully the choice of indicator in relation to the liquid under examination. For turbid liquids there are the so-called "achromatic indicators," which are mixtures of indicators so chosen that the middle point of the colour change in one is complementary to that of the other, the resulting transition point of the mixed indicator being grey.[30] As an example, a mixture of bromocresol-green, neutral-red, and phenolphthalein indicates sharply at p_H 4·5 and 8·5, and is therefore available for the titration of phosphoric acid.

An interesting method of identifying a solid when the melting point cannot be used because of decomposition, depends upon determining the b. p. of the saturated solution in a suitable apparatus. If the solid under test is the same as the solute, then the b. p. of the

[26] F. R. McCrumb, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 233; *A.*, 1023.

[27] M. G. Mellon and G. W. Ferner, *J. Physical Chem.*, 1931, **35**, 1025.

[28] N. V. Sidgwick and L. A. Woodward, *Proc. Roy. Soc.*, 1930, [*A*], **130**, 1.

[29] J. W. McBain, (Miss) M. E. Laing, and O. E. Clark, *J. Gen. Physiol.*, 1929, **12**, 695.

[30] E. L. Smith, *Quart. J. Pharm.*, 1930, 499; *A.*, 184.

saturated solution will not be affected on addition of the unknown substance. With due precautions the procedure is available likewise for ascertaining the purity of a substance.[31]

A problem which is sometimes of considerable importance in analysis is the determination of the density of solids when small quantities only are available. Heavy liquids of suitable range are not always available for the denser materials. A device is described which gives satisfactory results with as little as 0·05 g. of solid, whether in the form of powder or massive.[32] This consists of a glass tube fitted with a capillary side arm on which there are two marks. The quantity of some suitable liquid, weighed from a weight burette, required to occupy the space between the two marks is ascertained. A determination can then be made readily, by filling the tube as far as the lower mark with the liquid, introducing a weighed portion of the solid, and then introducing sufficient liquid to fill the instrument to the second mark from the weight burette. It is obvious that the weight of liquid displaced by the solid can be found with some accuracy provided precautions be taken to reduce vaporisation when volatile liquids are used.

The discovery that per-rhenates of certain organic bases, *e.g.*, " nitron," give insoluble compounds is of much value for determining the element. Rhenium sulphide may be precipitated from a hot solution of a rhenium salt acidified with hydrochloric acid. The precipitation is rather slow, but the insoluble sulphide is easily converted into per-rhenate by suspending it in sodium hydroxide solution and adding hydrogen peroxide. From an acetic acid solution the rhenium can be obtained quantitatively as nitron per-rhenate.[33] The sulphide reaction is delicate, and the precipitation with nitron is nearly complete, particularly if nitron acetate is present.[34] A difficulty arises from the co-precipitation by nitron of any molybdenum present in the solution. Fortunately, molybdenum can be removed as $MoO_2(C_9H_6ON)_2$ by the use of 8-hydroxyquinoline in acetic acid solution, leaving the rhenium in solution.[35] The separation of the bulk of the molybdenum may be effected by distillation of rhenium chloride at 175—200° from a sulphuric acid solution of the per-rhenate. The precipitation of the remaining molybdenum by hydroxyquinoline can then be carried out.[35a] An alternative method of estimating rhenium takes advantage of the

[31] J. O. Halford, *J. Amer. Chem. Soc.*, 1931, **53**, 2640; *A.*, 1022.
[32] E. W. Blank, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 9; *A.*, 456.
[33] W. Geilmann and F. Weibke, *Z. anorg. Chem.*, 1931, **195**, 289; *A.*, 328.
[34] W. Geilmann and A. Voigt, *ibid.*, 1930, **193**, 311; *A.*, 1930, 1547.
[35] W. Geilmann and F. Weibke, *ibid.*, 1931, **199**, 347; *A.*, 1143.
[35a] *Idem, ibid.*, p. 120; *A.*, 1025.

insolubility of thallous per-rhenate [35b] from a solution acidified with acetic acid. The thallous per-rhenate is weighed after being dried at 140°, but the results are somewhat low, most likely owing to volatilisation.

Inorganic Analysis.

Qualitative.—The sensitivity of certain tests is increased by shaking the aqueous solution with an immiscible liquid,[36] and by observation under strong illumination.[37] Schemes are proposed for the systematic detection of the commoner kations,[38] and certain anions,[39] using 0·1-g. samples. A detailed summary has been made of the application of organic reagents to mineral qualitative analysis;[40] the sensitivity of such reagents generally increases with their molecular weight.[41] Notes are given for the detection of traces of chromate in presence of permanganate, of hydrogen sulphide in water,[42] and of nickel in cobalt salts,[43] and further observations are made on the detection of certain heavy metals with diphenylthiocarbazide.[44] Quinoline [45] and hexamethylenetetramine, ammonia, and hydrazine,[46] have been applied as microchemical reagents; certain metals afford colour reactions with ammonia in presence of resorcinol,[47] and the properties of hydroxylamine as a precipitant have been examined.[48]

Ammoniacal picric acid gives characteristic crystalline precipitates with copper and some other heavy metals; [49] 2 : 7-diaminofluorene can serve as reagent for copper, zinc, and cadmium,[50] and " direct-

[35b] F. Krauss and H. Steinfeld, *Z. anorg. Chem.*, 1931, **197**, 52; *A.*, 589.

[36] I. Stone, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 325; *A.*, 1022; see also Feigl and others, *Mikrochem.*, 1931, **9**, 165; *A.*, 590.

[37] W. Böttger and B. M. Schall, *ibid.*, Emich Festschr., 1930, 29; *A.*, 1930, 1545.

[38] A. Scheinkmann, *Z. anal. Chem.*, 1931, **83**, 176; **85**, 344; *A.*, 587, 1260; C. J. van Nieuwenberg, *Mikrochem.*, 1931, **9**, 199; *A.*, 698.

[39] *Idem, ibid.*; S. I. Dijatschkovski and T. I. Isaenko, *J. Gen. Chem. Russia*, 1931, **1**, 81; *A.*, 925.

[40] B. Tougarinoff, *Ann. Soc. Sci. Bruxelles*, 1930, **50**, [*B*], 145; *A.*, 188.

[41] V. V. Tamchyna, *Mikrochem.*, 1931, **9**, 229; *A.*, 701.

[42] F. Feigl, *ibid.*, Emich Festschr., 1930, 125; *A.*, 1930, 1547.

[43] *Idem, ibid.*; F. Feigl and H. J. Kapulitzas, *Z. anal. Chem.*, 1930, **82**, 417; *A.*, 455.

[44] H. Fischer, *Mikrochem.*, 1930, **8**, 319; *A.*, 328.

[45] I. M. Korenman, *Pharm. Zentr.*, 1930, **71**, 769; *A.*, 1931, 188.

[46] P. Rây and P. B. Sarkar, *Mikrochem.*, Emich Festschr., 1930, 243; *A.*, 1930, 1544.

[47] L. Bey, *Bull. Soc. chim.*, 1930, [iv], **47**, 1192; *A.*, 1930, 1545.

[48] J. C. Roldán, *Anal. Fis. Quím.*, 1930, **28**, 1080; *A.*, 1930, 1547.

[49] I. M. Korenman, *Pharm. Zentr.*, 1931, **72**, 225; *A.*, 701: *J. Chem. Ind. Russia*, 1931, **8**, 276; *A.*, 927.

[50] J. Schmidt and W. Hinderer, *Ber.*, 1931, **64**, [*B*], 1793; *A.*, 1045.

green B" for copper.[51] Boiling potassium cyanide solution dissolves zinc, but not cadmium cyanide; [52] methods are described for the detection of copper,[53] zinc and silver,[54] bismuth,[55] and cadmium.[56]

The elements of the aluminium group are separated from those of the iron group by boiling the nitric acid solution with sodium carbonate, hydroxide, and peroxide; [57] 2 : 2′-dipyridyl in slightly acid solution is a sensitive test for ferrous salts, with which it gives a red coloration.[58] Reactions of simple and complex iron compounds have been investigated.[59] The detection of chromium [60] and of manganese [61] in minerals and rocks is described, as also a number of methods for cobalt, as cæsium cobaltinitrite,[62] with sodium thiosulphate,[63] with thioglycollanilide,[64] and with eriochrome blue-black B and red B.[65]

p-Nitrobenzeneazoresorcinol, besides being a specific reagent for magnesium,[66] is a useful indicator over the range p_H 10·8—13·0; a number of other dyes has been investigated, but in all cases cobalt and nickel give the same reactions as magnesium.[67] For the microchemical detection of sodium, a uranyl acetate solution is used; [68] modifications of the triple acetate test have been made.[69]

Molybdic acid gives a violet coloration with potassium cetyl-

[51] P. Sisley and David, *Bull. Soc. chim.*, 1930, [iv], **47**, 1188; *A.*, 1930, 1546.

[52] N. A. Tananaev and N. S. Fedulov, *Ukraine Chem. J.*, 1930, **5**, (Sci.), 213; *A.*, 327.

[53] K. M. Filimonovitsch, *ibid.*, p. 383; *A.*, 927; A. Sergeev, *ibid.*, p. 227; *A.*, 327.

[54] A. Sergeev, *loc. cit.*

[55] G. Lochmann, *Z. anal. Chem.*, 1931, **85**, 841; *A.*, 1262.

[56] J. S. Pierce and W. T. Forsee, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 188; *A.*, 701.

[57] S. Ato, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1930, **14**, 287; *A.*, 454.

[58] F. Feigl and H. Hamburg, *Z. anal. Chem.*, 1931, **86**, 7; *A.*, 1261.

[59] O. Baudisch, *Biochem. Z.*, 1931, **232**, 35; *A.*, 589.

[60] H. Leitmeier and F. Feigl, *Tsch. Min. Petr. Mitt.*, 1931, **41**, 95; *A.*, 455.

[61] H. Leitmeier, *ibid.*, p. 87; *A.*, 454.

[62] H. Yagoda and H. M. Partridge, *J. Amer. Chem. Soc.*, 1930, **52**, 4857; *A.*, 329.

[63] M. G. de Celis, *Anal. Fís. Quím.*, 1931, **29**, 262; *A.*, 814.

[64] T. Bersin, *Z. anal. Chem.*, 1931, **85**, 428; *A.*, 1262.

[65] E. Eegriwe, *ibid.*, 1930, **82**, 150; *A.*, 1930, 1547.

[66] J. V. Dubský and A. Okáč, *Chem. Listy*, 1930, **24**, 492; *A.*, 327; I. Stone, *Science*, 1930, **72**, 322; *A.*, 56.

[67] I. M. Kolthoff, *Mikrochem.*, Emich Festschr., 1930, 180; *A.*, 1930, 1544.

[68] A. Martini, *ibid.*, 1931, **9**, 422; *A.*, 926.

[69] P. Feldstein and A. M. Ward, *Analyst*, 1931, **56**, 245; *A.*, 587; R. Montequi and R. de Sádaba, *Anal. Fís. Quím.*, 1931, **29**, 255; *A.*, 812.

xanthate; [70] delicate tests for zirconium [71] and germanium [72] are described, as also observations on Feigl's rhodanine reagent for silver, which gives colorations with gold and palladium.[73]

Limits are given for the sensitivity of the colour reaction of free halogens with *p*-aminodimethylaniline.[74] A drop test for the detection of bromides depends on the formation of eosin from fluorescein; [75] preferential precipitation of silver chloride is utilised for detecting chlorides in presence of bromide.[76] Chlorates produce an opalescence when shaken with saturated aqueous hydrogen sulphide, whereas perchlorates and nitrates do not.[77] Addition of a solution of benzidine acetate to one of a fluoride in presence of mercuric acetate affords, under certain conditions, a yellow precipitate.[78]

A drop method for detecting ferrocyanide when alone [79] or in presence of thiocyanate [80] is described. Capillary tubes are recommended for storing reagents such as diphenylamine which are unstable in solution; the 2 : 4-diamino-6-hydroxypyrimidine reaction may be applied to the microdetection of nitrite.[81] The reaction of nitric acid with diphenylbenzidine follows a course similar to that with diphenylamine, but the colour is about twice as intense and much more affected by excess of reagent.[82] A reaction with an acid-alcoholic solution of vanillin occurs with hydrogen peroxide or perborates.[83]

Quantitative.—Tartrazine and phenosafranine are shown to be suitable adsorption indicators for the mutual titration of chloride or bromide with silver nitrate.[84] Several papers deal with electro-

[70] J. V. Tamchyna, *Chem. Listy*, 1930, **24**, 465; *A.*, 329.

[71] F. Pavelka, *Mikrochem.*, 1930, **8**, 345; *A.*, 329; F. Feigl, P. Krumholz, and E. Rajmann, *ibid.*, 1931, **9**, 395; *A.*, 928.

[72] W. Geilmann and K. Brünger, *Z. anorg. Chem.*, 1931, **196**, 312; *A.*, 455.

[73] F. Feigl and H. Leitmeier, *Tsch. Min. Petr. Mitt.*, 1931, **41**, 188; *A.*, 701; F. Feigl, P. Krumholz, and E. Rajmann, *Mikrochem.*, 1931, **9**, 165; *A.*, 590.

[74] H. E. Tremain, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 225; *A.*, 699.

[75] A. V. Pavlinova, *Ukraine Chem. J.*, 1930, **5**, (Sci.), 231; *A.*, 325.

[76] G. G. Longinescu and T. I. Pirtea, *Bull. Acad. Sci. Roumaine*, 1930, **13**, 195; *A.*, 185.

[77] T. P. Raikova-Kovatscheva, *Z. anal. Chem.*, 1930, **82**, 415; *A.*, 451.

[78] C. Pertusi, *Atti III Cong. Naz. Chim.*, 1929, 573; *A.*, 925.

[79] A. V. Pavlinova and T. N. Bach, *Ukraine Chem. J.*, 1930, **5**, (Sci.), 235; *A.*, 326.

[80] *Idem*, *ibid.*, p. 233; *A.*, 326.

[81] F. L. Hahn, *Mikrochem.*, Emich Festschr., 1930, 143; *A.*, 1930, 1542.

[82] H. Riehm, *Z. anal. Chem.*, 1930, **81**, 439; *A.*, 1930, 1542.

[83] C. Griebel, *Mikrochem.*, 1931, **9**, 313; *A.*, 925.

[84] A. J. Berry and P. T. Durrant, *Analyst*, 1930, **55**, 613; *A.*, 56.

metric methods for ascertaining p_H[85] and with oxidation–reduction indicators.[86] Sixteen dyes of different colours have been selected as suitable internal indicators in volumetric bromate reactions.[87]

The manner in which the chlorine ion contaminates a number of precipitates shows that three types of precipitation process may be recognised.[88] Despite criticism,[89] J. Dick upholds his method for the rapid drying of precipitates [90] and extends it to a number of others.[91] A white rod and much indicator are used for the titration of dark-coloured liquids.[92] The technique of accurate volumetric analysis as applied to delicate work,[93] the sources of error in micro-acidimetric titrations,[94] the factors affecting determinations with the centrifuge,[95] and the analytical significance of ageing phenomena [96] are discussed.

The benzidine reaction for " active " iron may also be used in alcoholic solution and is most sensitive at p_H 3·95.[97] The presence of more than 5% of iron prevents the removal of phosphate by boiling with a nitric acid solution of stannous nitrate.[98]

Errors in the determination of water by drying are discussed; [99] other methods involve decomposition of α-naphthyloxychloro-

[85] R. J. Fosbinder, *J. Lab. Clin. Med.*, 1931, **16**, 411; *A.*, 811; I. M. Kolthoff and T. Kameda, *J. Amer. Chem. Soc.*, 1931, **53**, 821; *A.*, 585; H. T. S. Britton and R. A. Robinson, *J.*, 1931, 458; *A.*, 585; P. Vignon, *J. Soc. Leather Trades' Chem.*, 1931, **15**, 367; *A.*, 1141; V. Morani, *Ann. Chim. Appl.*, 1931, **21**, 83; *A.*, 450; S. O. Rawling and G. B. Harrison, *Phot. J.*, 1931, **71**, 108; *A.*, 450; M. Kilpatrick, jun., and E. F. Chase, *J. Amer. Chem. Soc.*, 1931, **53**, 1732; *A.*, 811; S. Stone, *Rec. trav. chim.*, 1930, **49**, 1133; *A.*, 184; B. Elema, *Chem. Weekblad*, 1931, **28**, 223, 234; *A.*, 699; H. T. S. Britton and E. N. Dodd, *J.*, 1931, 829; *A.*, 699.

[86] I. M. Kolthoff and L. A. Sarver, *J. Amer. Chem. Soc.*, 1930, **52**, 4179; *A.*, 54; J. Knop, *Z. anal. Chem.*, 1931, **85**, 253; *A.*, 1256; L. Michaelis, *J. Biol. Chem.*, 1931, **91**, 369; *A.*, 687.

[87] G. F. Smith and H. H. Bliss, *J. Amer. Chem. Soc.*, 1931, **53**, 2091; *A.*, 925.

[88] Z. Karaoglanov and B. Sagortschev, *Z. anorg. Chem.*, 1931, **198**, 352; *A.*, 926.

[89] L. Moser and L. von Zombory, *Z. anal. Chem.*, 1930, **81**, 95; *A.*, 1930, 1149.

[90] *Ibid.*, 1931, **83**, 105; *A.*, 584.

[91] *Idem, ibid.*, 1930, **82**, 401; *A.*, 453.

[92] E. Rossmann, *Chem.-Ztg.*, 1931, **55**, 403; *A.*, 810.

[93] W. Ponndorf, *Z. anal. Chem.*, 1931, **84**, 289; **85**, 1; *A.*, 1022, 1259.

[94] J. Mika, *Mikrochem.*, 1931, **9**, 143; *A.*, 584; *Z. anal. Chem.*, 1931, **86**, 54; *A.*, 1256.

[95] H. S. Greene, *J. Amer. Chem. Soc.*, 1931, **53**, 3275; *A.*, 1256.

[96] H. Fischer, *Z. angew. Chem.*, 1930, **43**, 919; *A.*, 1930, 1541.

[97] A. Simon and T. Reetz, *Z. anorg. Chem.*, 1930, **194**, 89; *A.*, 57.

[98] A. Krüger, *Z. anal. Chem.*, 1930, **82**, 62; *A.*, 57.

[99] M. Dolch and K. Büche, *Pflanzenbau*, 1930, **4**, 64; *A.*, 1023.

phosphine,[1] distillation with chlorinated hydrocarbons,[2] and ebullioscopic procedure with methyl alcohol or acetone.[3] Formulæ are derived for calculating the state of combination of the constituents in mineral waters based on the dissociation constants of the acid radicals present and the p_H of the water;[4] methods are given for the determination of fluorine,[5] cæsium and rubidium,[6] and arsenic, molybdenum, and bismuth [7] in mineral waters.

Arsenite solutions are best prepared by dissolving arsenious oxide in carbonate-free sodium bicarbonate solution.[8] Sulphates of such aromatic amines as aniline and toluidine serve satisfactorily as standards in alkalimetry;[9] perchloric acid is similarly applied.[10] Standardisation of thiosulphate solution by means of ceric sulphate is described.[11]

Microchemical methods are applied to the determination of traces of various metals, of hydrogen and carbon monoxide in iron, and of metallic carbonyls in air;[12] the determinations and separations of the metals of the hydrogen sulphide group have been critically studied,[13] as has also the separation of lead from barium, strontium, and calcium sulphate with ammonium acetate.[14] Conditions are given for the quantitative separation of lead as chromate from iron,[15] bismuth,[16] mercury and copper;[17] precipitation as

[1] E. Dittler and H. Hueber, *Z. anorg. Chem.*, 1931, **195**, 41; *A.*, 325; *ibid.*, **199**, 17; *A.*, 1023; J. Lindner, *Z. anal. Chem.*, 1931, **86**, 141; *A.*, 1257.

[2] T. R. Fairbrother and R. J. Wood, *Ind. Chem.*, 1930, **6**, 442; *A.*, 185; H. Lundin, *Chem.-Ztg.*, 1931, **55**, 762; *A.*, 1256; G. Middleton, *Pharm. J.*, 1931, **127**, 86; *A.*, 1023.

[3] S. Bakowski, *Rocz. Chem.*, 1931, **11**, 49, 269, 490; *A.*, 585, 811, 1023.

[4] L. Fresenius and O. Fuchs, *Z. anal. Chem.*, 1930, **82**, 226; *A.*, 1930, 1541.

[5] J. Casares and R. Casares, *Anal. Fis. Quim.*, 1930, **28**, 1159; *A.*, 55.

[6] L. Fresenius, *Z. anal. Chem.*, 1931, **86**, 182; *A.*, 1256.

[7] O. Steiner, *ibid.*, 1930, **81**, 389; *A.*, 1930, 1541.

[8] I. Tananaev, *Ukraine Chem. J.*, 1930, **5**, (Sci.), 217; *A.*, 326.

[9] E. Strasser, *Z. anal. Chem.*, 1930, **82**, 114; *A.*, 1930, 1541.

[10] G. F. Smith and W. W. Koch, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 52; *A.*, 450; see also G. F. Smith and O. E. Goehler, *ibid.*, p. 61; *A.*, 451.

[11] N. H. Furman and J. H. Wallace, jun., *J. Amer. Chem. Soc.*, 1931, **53**, 1283; *A.*, 700.

[12] R. Lucas, F. Grassner, and E. Neukirch, *Mikrochem.*, Emich Festschr., 1930, 197; *A.*, 1930, 1546.

[13] P. Wenger and C. Cimerman, *Helv. Chim. Acta*, 1931, **14**, 718; *A.*, 1261.

[14] I. Majdel, *Arhiv Hemiju*, 1930, **4**, 76; *A.*, 1930, 1544; *Z. anal. Chem.*, 1931, **83**, 36; *A.*, 453; F. Feigl and L. Weidenfeld, *ibid.*, **84**, 220; *A.*, 926; W. W. Scott and S. M. Alldredge, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 32; *A.*, 453.

[15] H. Funk and O. von Zur-Mühlen, *Z. anal. Chem.*, 1931, **85**, 435; *A.*, 1260.

[16] H. Funk and J. Weinzierl, *ibid.*, 1930, **81**, 380; *A.*, 1930, 1545.

[17] H. Funk and J. Schormüller, *ibid.*, **82**, 361; *A.*, 187.

chromate from dilute perchloric acid is recommended.[18] Neutral solutions of lead salts may be titrated with molybdate [19] or sodium carbonate.[20] The oxychloride is preferred for the separation of bismuth from lead; [21] lead and bismuth may be titrated by the filtration method [22] previously used for calcium, magnesium, etc.[23] Cadmium may be determined gravimetrically or volumetrically by means of ammonium molybdate.[24] Further observations have been made on the use of salicylaldoxime as a reagent for copper; [25] its place may be taken, though without advantage, by various structurally-related compounds.[26] Separation of copper from cadmium may be effected with gallic acid [27] or potassium formate,[28] and from zinc with iodide and thiosulphate.[29] Among volumetric methods for copper, the iodide [30] and one involving permanganate oxidation following precipitation by Spacu's reaction have received attention.[31] Copper and titanium are precipitated from slightly acid solution by 5 : 7-dibromo-8-hydroxyquinoline.[32]

The precipitated mercuric sulphide obtained directly from acid solution is excessive; [33] a method is evolved, particularly for organic compounds, involving distillation as mercuric chloride in a stream of gaseous hydrogen chloride.[34] Volumetric methods are described for mercuric cyanide [35] and mercurous chloride,[36] and

[18] D. J. Brown, J. A. Moss, and J. B. Williams, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 134; *A.*, 701.

[19] R. C. Wiley, P. M. Ambrose, and A. D. Bowers, *ibid.*, 1930, **2**, 415; *A.*, 1930, 1545.

[20] S. Komaretzky, *Z. anal. Chem.*, 1931, **84**, 407; *A.*, 1024; E. Benesch and E. Erdheim, *Przemysł Chem.*, 1931, **15**, 153; *A.*, 701.

[21] W. Hertel, *Metall u. Erz*, 1930, **27**, 557; *A.*, 588.

[22] H. T. Bucherer and F. W. Meier, *Z. anal. Chem.*, 1931, **83**, 351; *A.*, 588.

[23] *Idem, ibid.*, 1930, **82**, 1; *B.*, 1930, 1153.

[24] R. C. Wiley, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 14; *A.*, 453.

[25] O. L. Brady, *J.*, 1931, 106; F. Ephraim, *Ber.*, 1931, **64**, [*B*], 1215; *A.*, 813 : W. Reif, *Mikrochem.*, 1931, **9**, 424; *A.*, 927.

[26] F. Ephraim, *Ber.*, 1931, **64**, [*B*], 1210; *A.*, 813.

[27] P. N. Das-Gupta and H. Saha, *J. Indian Chem. Soc.*, 1931, **8**, 19; *A.*, 813.

[28] E. I. Fulmer, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 257; *A.*, 1025.

[29] H. Brintzinger, *Z. anal. Chem.*, 1931, **86**, 157; *A.*, 1260.

[30] R. Intonti, *Ann. Chim. Appl.*, 1930, **20**, 583; *A.*, 187; B. Park, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 77; *A.*, 454.

[31] J. Golse, *Bull. Soc. chim.*, 1931, [iv], **49**, 84; *A.*, 454 : L. Cuny, *J. Pharm. Chim.*, 1931, [viii], **13**, 513; *A.*, 813.

[32] R. Berg and H. Küstenmacher, *Mikrochem.*, Emich Festschr., 1930, 26; *A.*, 1930, 1546.

[33] E. P. Fenimore and E. C. Wagner, *J. Amer. Chem. Soc.*, 1931, **53**, 2453; *A.*, 1025.

[34] *Idem, ibid.*, p. 2461; *A.*, 1025.

[35] E. Cattelain, *J. Pharm. Chim.*, 1930, [viii], **12**, 529; *A.*, 187.

[36] D. Köszegi, *Pharm. Ztg.*, 1931, **76**, 524; *A.*, 813.

Denigès's cyanide method has been modified.[37] The importance of determining minute traces of mercury is again emphasised.[38]

Bismuth, aluminium, and zinc, precipitated by 8-hydroxyquinoline are determined colorimetrically with a phosphotungstomolybdate reagent; [39] a method has been devised for determining small quantities of bismuth in organs without decomposing them.[40] Reduction of stannic salts by lead [41] and of antimony also by hypophosphorous acid [42] prior to titration have been examined, particularly as regards the interfering effects of other metals; reduction with iron powder for small amounts of tin is preferred to aluminium.[43] Some notes on the Gutzeit arsenic test are recorded; [44] conditions are given for the use of iodide catalyst in the titration of arsenious acid and permanganate.[45]

Diphenylaminesulphonic acid is recommended as indicator for the titration of iron, especially as tungstate does not interfere,[46] despite its larger correction.[47] Further data are recorded on the practical applications of Knop's original method; [48] *p*-phenetidine has also been used as the indicator,[49] and on the micro-scale, various triphenylmethane dyes.[50] The oxidation of ferrous iron by iodine in presence of phosphate proceeds slowly to completion.[51] Iron may be separated from manganese by hydrazine hydrate,[52] from cobalt by various mercury-ammonium derivatives,[53] and from zinc, manganese, etc., by hexamethylenetetramine.[54]

[37] O. Pročke, *Coll. Czech. Chem. Comm.*, 1930, **2**, 593; *A.*, 1930, 1546.

[38] A. Stock, *Naturwiss.*, 1931, **19**, 499; *A.*, 1025; A. Stock, H. Lux, F. Cucuel, and F. Gerstner, *Z. angew. Chem.*, 1931, **44**, 200; *A.*, 588; B. L. Moldavski, *J. Appl. Chem. Russia*, 1930, **3**, 955; *A.*, 589.

[39] M. Teitelbaum, *Z. anal. Chem.*, 1930, **82**, 366; *A.*, 188.

[40] N. A. Valiaschko and P. K. Virup, *Ukraine Chem. J.*, 1930, **5**, (Sci.), 275; *A.*, 702.

[41] S. G. Clarke, *Analyst*, 1931, **56**, 82; *A.*, 590.

[42] B. S. Evans, *ibid.*, p. 171; *A.*, 590.

[43] R. Höltje, *Z. anorg. Chem.*, 1931, **198**, 287; *A.*, 928.

[44] T. J. Ward, *Analyst*, 1930, **55**, 630; *A.*, 55; J. P. Mayrand, *J. Amer. Pharm. Assoc.*, 1931, **20**, 637; *A.*, 1024.

[45] R. Lang, *Z. anal. Chem.*, 1931, **85**, 176; *A.*, 1258.

[46] L. A. Sarver and I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1931, **53**, 2902; *A.*, 1141.

[47] *Idem, ibid.*, p. 2906; *A.*, 1141.

[48] C. J. Schollenberger, *ibid.*, p. 88; *A.*, 328; O. Rothe and A. P. Sobrinho, *Rev. brasil. Chim.*, 1929, **1**, 129; *A.*, 814.

[49] L. Szebellédy, *Magyar Chem. Fol.*, 1930, **36**, 40; *A.*, 188.

[50] J. Knop and O. Kubelková, *Z. anal. Chem.*, 1931, **85**, 401; *A.*, 1261.

[51] W. D. Bonner and H. Romeyn, jun., *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 85; *A.*, 454.

[52] A. Jílek and V. Vicovský, *Coll. Czech. Chem. Comm.*, 1931, **3**, 379; *A.*, 1261.

[53] B. Šolaja and V. Matovinović, *Arhiv Hemiju*, 1931, **5**, 232; *A.*, 1260.

[54] P. Rây, A. K. Chattopadhya, and D. Bhaduri, *Z. anal. Chem.*, 1931, **86**, 13; *A.*, 1261.

If iron and nickel are present, a single treatment with hypobromite does not suffice to oxidise chromium salts completely,[55] but they can be so oxidised by perchloric acid.[56] Observations are made on the determination of the oxide content of aluminium,[57] and on the precipitation of aluminium, chromium, and iron by potassium cyanate.[58] Aluminium may be precipitated by hydrazine carbonate.[59]

The precipitation of manganese salts by water-soluble carbonates,[60] the oxidation by persulphate in presence of silver salts,[61] and precipitation as manganese ammonium phosphate [62] have been examined. Precautions to be observed during precipitation of cobalt [63] and nickel [64] as sulphide and subsequent conversion into metal and oxide respectively are enumerated, and also in the cobalt thiocyanate colorimetric comparison.[65]

A scheme for the determination of zinc combined in mixtures as oxide, silicate, ferrite, sulphate, and sulphide is presented.[66] Small concentrations of lead do not interfere with the precipitation of small quantities of zinc by 8-hydroxyquinoline.[67]

Following precipitation of oxalate, an alkalimetric titration is applied to small amounts of calcium.[68] Calcium, barium, and strontium, present in pairs, are separated by the varying solubility of their bromides in *iso*butyl alcohol.[69] For precipitation of calcium as oxalate in presence of arsenate, a slight excess of ammonia at high temperature is recommended.[70] For micro-determination,

[55] E. Schulek and A. Dózsa, *Z. anal. Chem.*, 1931, **86**, 81; *A.*, 1262.

[56] L. H. James, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 258; *A.*, 1026.

[57] A. M. Shandorov, *Tzvet. Met.*, 1930, 672; *A.*, 813: H. Löwenstein, *Z. anorg. Chem.*, 1931, **199**, 48; *A.*, 1025.

[58] B. J. F. Dorrington and A. M. Ward, *Analyst*, 1930, **55**, 625; *A.*, 56.

[59] A. Jílek and J. Lukas, *Chem. Listy*, 1930, **24**, 365; *A.*, 1930, 1547.

[60] *Idem*, *ibid.*, 1931, **25**, 225, 249; *A.*, 927; *Coll. Czech. Chem. Comm.*, 1931, **3**, 187; *A.*, 702.

[61] R. Lang and F. Kurtz, *Z. anal. Chem.*, 1931, **85**, 181; *A.*, 1261; J. H. van der Meulen, *Chem. Weekblad*, 1931, **28**, 377; *A.*, 927.

[62] P. Nuka, *Latvij. Univ. Raksti*, 1931, **2**, 1; *A.*, 1142.

[63] M. M. Haring and M. Leatherman, *J. Amer. Chem. Soc.*, 1930, **52**, 5135; *A.*, 325.

[64] M. M. Haring and B. B. Westfall, *ibid.*, p. 5141; *A.*, 325.

[65] E. S. Tomula, *Z. anal. Chem.*, 1931, **83**, 6; *A.*, 454.

[66] V. Tafel and G. Sille, *Z. angew. Chem.*, 1930, **43**, 948; *A.*, 1930, 1545; 1931, **44**, 792; *A.*, 1260.

[67] M. E. Stas, *Pharm. Weekblad*, 1931, **68**, 93; *A.*, 453.

[68] C. H. Fiske and E. T. Adams, *J. Amer. Chem. Soc.*, 1931, **53**, 2498; *A.*, 1024; C. H. Fiske and M. A. Logan, *J. Biol. Chem.*, 1931, **93**, 211; *A.*, 1342.

[69] L. Szebellédy, *Magyar Chem. Fol.*, 1929, **35**, 59, 63, 100; *A.*, 186, 187.

[70] J. T. Dobbins and W. M. Mebane, *J. Amer. Chem. Soc.*, 1930, **52** 4285; *A.*, 56.

calcium is precipitated as triple nitrite with potassium and nickel,[71] as oxalate,[72] or as picrolonate; [73] a method in which calcium and magnesium are titrated in the same solution is specially suited for the analysis of dolomite.[74] Calcium may conveniently be separated from magnesium by precipitation as molybdate.[75] Direct volumetric methods for barium depend upon the use of sodium rhodizonate as indicator [76] and upon the fact that potassium chromate reacts alkaline to bromothymol-blue and phenol-red.[77] Various methods of determination of strontium and of its separation from calcium are reviewed.[78] Investigations on magnesium may be divided into those using phosphate [79] and those involving use of 8-hydroxyquinoline.[80]

Various modifications and adaptations of the triple acetate method for sodium [81] and the cobaltinitrite method for potassium [82] have been made. The direct sulphate method gives low results in the presence of 5-substituted barbituric acids.[83] Other methods

[71] M. Mousseron, *Bull. Soc. Chim. biol.*, 1930, **12**, 1014; *A.*, 1930, 1543; *ibid.*, 1931, **13**, 831; *A.*, 1259.

[72] L. Velluz and R. Deschaseaux, *ibid.*, p. 797; *A.*, 1259; *Compt. rend. Soc. Biol.*, 1930, **104**, 976; *A.*, 588.

[73] R. Dvorzak and W. Reich-Rohrwig, *Z. anal. Chem.*, 1931, **86**, 98; *A.*, 1259.

[74] K. L. Maliarov, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 1529; *A.*, 56; *Mikrochem.*, 1931, **9**, 132; A., 588; compare also G. A. Pantschenko, *Ukraine Chem. J.*, 1930, **5**, (Sci.), 187; *A.*, 327.

[75] R. C. Wiley, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 127; *A.*, 701.

[76] L. Zombory, *Magyar Chem. Fol.*, 1929, **35**, 90; *A.*, 187.

[77] S. Balachovski, *Z. anal. Chem.*, 1930, **82**, 206; *A.*, 1930, 1544.

[78] W. Noll, *Z. anorg. Chem.*, 1931, **199**, 193; *A.*, 1259.

[79] J. I. Hoffman and G. E. F. Lundell, *Bur. Stand. J. Res.*, 1930, **5**, 279; *A.*, 55; M. Javillier and D. Djelatides, *Ann. Falsif.*, 1931, **24**, 133; *A.*, 701; V. Njegovan and V. Marjanović, *Arhiv Hemiju*, 1931, **5**, 243; *A.*, 1259; *idem*, *Z. anal. Chem.*, 1930, **82**, 154; *A.*, 1930, 1544; J. Majdel, *ibid.*, p. 425; *A.*, 452.

[80] J. C. Redmond and H. A. Bright, *Bur. Stand. J. Res.*, 1931, **6**, 113; *B.*, 396; F. L. Hahn, *Z. anal. Chem.*, 1931, **86**, 153; *A.*, 1259; W. A. Hough and J. B. Ficklen, *J. Amer. Chem. Soc.*, 1930, **52**, 4752; *A.*, 327; K. Nehring, *Z. Pflanz. Düng.*, 1931, **21**, [*A*], 300; *A.*, 1142; R. Berg, W. Wolker, and E. Skopp, *Mikrochem.*, Emich Festschr., 1930, 18; *A.*, 1930, 1546.

[81] A. M. Butler and E. Tuthill, *J. Biol. Chem.*, 1931, **93**, 171; *A.*, 1342; J. T. Dobbins and R. M. Byrd, *J. Amer. Chem. Soc.*, 1931, **53**, 3288; *A.*, 1259; E. R. Caley and D. V. Sickman, *ibid.*, 1930, **52**, 4247; *A.*, 56; A. Blenkinsop, *J. Agric. Sci.*, 1930, **20**, 511; *A.*, 186; R. A. McCance and H. L. Shipp, *Biochem. J.*, 1931, **25**, 449; *A.*, 926.

[82] J. Fischer, *Biochem. Z.*, 1931, **238**, 148; *A.*, 1259; R. A. Herzner, *ibid.*, **237**, 129; *A.*, 1259; P. J. Van Rysselberge, *Ind. Eng. Chem.* (*Anal.*), 1921, **3**, 3; *A.*, 452; P. N. Grigoriev and S. S. Korol, *J. Chem. Ind.*, *Russia*, 1931, **8**, 68; *A.*, 700.

[83] G. W. Collins, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 291; *A.*, 1024.

for potassium depend upon titration of the acid tartrate,[84] upon colorimetric comparison of the picrate,[85] and upon the use of lithium chloroplatinate.[86] To convert alkali sulphates into chlorides in silicate analysis, they are heated with hydrazine hydrochloride; [87] small quantities of alkalis are separated from acids insoluble in water, *e.g.*, tungstic acid, by electrodialysis.[88]

Beryllium may be separated from aluminium by means of guanidine carbonate; [89] the sulphite process of separating these two elements has been reinvestigated,[90] and further details given for the microanalysis of beryllium silicate rocks.[91] For low concentrations of titanium, accurate results by the colorimetric method are obtainable by comparing solutions of identical colour.[92] Further separations of gallium by means of camphoric acid are recorded.[93] For molybdenum, the permanganometric method [94] and precipitation as lead molybdate [95] have been examined. In the presence of molybdate, tungsten is determined colorimetrically by means of rhodamine-B, otherwise a quinol sulphate solution may be used.[96] Potassium chloride acts as an anti-oxidant, enabling manipulation of uranous compounds to be carried out within an hour or so in the presence of air; [97] zirconium is quantitatively precipitated by excess of selenious acid from hot slightly acid solutions.[98] In the series of investigation on the analytical chemistry of tantalum, niobium, and their mineral associates, a detailed technique is described [99] and also the separation of titanium from zirconium and hafnium.[1] Quantitative conversion of lanthanum oxalate into oxide does not occur below 800°; coprecipitation of basic

[84] L. Clarke and J. M. Davidson, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 324; *A.*, 1024.

[85] E. R. Caley, *J. Amer. Chem. Soc.*, 1931, **53**, 539, *A.*, 452.

[86] G. F. Smith and A. C. Shead, *ibid.*, p. 947; *A.*, 587.

[87] W. Mylius, *Sprechsaal*, 1930, **63**, 972; *A.*, 700.

[88] G. Heyne, *Z. angew. Chem.*, 1931, **44**, 328; *A.*, 926.

[89] A. Jílek and J. Kot̆a, *Coll. Czech. Chem. Comm.*, 1931, **3**, 336; *A.*, 1024.

[90] A. Travers and Schnoutka, *Compt. rend.*, 1931, **192**, 285; *A.*, 452.

[91] H. Thurnwald and A. A. Benedetti-Pichler, *Mikrochem.*, 1931, **9**, 324; *A.*, 927.

[92] H. Ginsberg, *Z. anorg. Chem.*, 1931, **198**, 162; *A.*, 814.

[93] S. Ato, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1931, **15**, 289; *A.*, 927.

[94] T. Döring, *Z. anal. Chem.*, 1930, **82**, 193; *A.*, 1930, 1548.

[95] H. A. Doerner, *Metal Ind.*, London, 1930, **37**, 444; *A.*, 589.

[96] G. Heyne, *Z. angew. Chem.*, 1931, **44**, 237; *A.*, 589.

[97] C. Ouellet, *Helv. Chim. Acta*, 1931, **14**, 967; *A.*, 1262.

[98] S. G. Simpson and W. C. Schumb, *J. Amer. Chem. Soc.*, 1931, **53**, 921; *A.*, 590.

[99] W. R. Schoeller, *Analyst*, 1931, **56**, 304; *A.*, 814.

[1] A. R. Powell and W. R. Schoeller, *ibid.*, 1930, **55**, 605; *A.*, 57.

chloride may be avoided by adding the lanthanum solution to a large excess of soda or ammonia.[2]

Full details are given of a procedure recommended for the determination of osmium.[3] Special attention has been given to the determination of small quantities of silver.[4] The chemical reactions of polonium are reviewed, with special reference to their analytical significance.[5]

Iodometric [6] and gravimetric [7] methods are described for the determination of small amounts of thallium, the former being applied particularly to organs.

The boric acid–alcohol flame coloration has been applied quantitatively.[8] Boric acid may be separated from dilute sulphuric acid solutions of heavy metal salts by distillation with methyl alcohol; [9] this process has been used for natural waters and plant materials.[10]

Carbon monoxide is oxidised to dioxide by a suspension of iodine pentoxide in oleum,[11] by copper oxide deposited on quartz,[12] and by silver oxide.[13] A number of modified methods of determining carbon dioxide are described; [14] the aniline method and the sodium iodide–acetone method have been adapted to give concordant results for carbonyl chloride in presence of other chlorine compounds.[15]

[2] I. M. Kolthoff and (Miss) R. Elmquist, *J. Amer. Chem. Soc.*, 1931, **53**, 1225; *A.*, 702.

[3] R. Gilchrist, *Bur. Stand. J. Res.*, 1931, **6**, 421; *A.*, 814.

[4] E. Schulek, *Mikrochem.*, Emich Festschr., 1930, 260; *A.*, 1930, 1543; J. Golse, *Bull. Soc. Pharm. Bordeaux*, 1930, **68**, 53; *A.*, 452 : C. Egg, *Schweiz. med. Woch.*, 1929, **59**, 84; *A.*, 186.

[5] M. Guillot, *J. Chim. physique*, 1931, **28**, 14; *A.*, 591.

[6] R. Fridli, *Magyar Gyó. Társas. Ért.*, 1929, **5**, 479; *A.*, 56; *Deut. Z. ges. gerichtl. Med.*, 1930, **15**, 478; *A.*, 328.

[7] L. Moser and W. Reif, *Mikrochem.*, Emich Festschr., 1930, 215; *A.*, 1930, 1545.

[8] W. Stahl, *Latvij. Univ. Raksti*, 1930, **1**, 369, 400; *A.*, 326; *Z. anal. Chem.*, 1931, **83**, 268, 340; *A.*, 587.

[9] E. Schulek and G. Vastagh, *ibid.*, 1931, **84**, 167; *A.*, 812.

[10] L. V. Wilcox, *Ind. Eng. Chem. (Anal.)*, 1930, **2**, 358; *A.*, 1930, 1543.

[11] H. A. J. Pieters, *Chem. Weekblad*, 1931, **28**, 335; *A.*, 812; *Z. anal Chem.*, 1931, **85**, 50; *A.*, 1258.

[12] A. Schmidt, *Z. angew. Chem.*, 1931, **44**, 152; *A.*, 926; H. A. J. Pieters, *Z. anal. Chem.*, 1931, **85**, 113; *A.*, 1258.

[13] *Idem, ibid.*; W. Manchot and G. Lehmann, *Ber.*, 1931, **64**, [*B*], 1261; *A.*, 926.

[14] C. A. Jacobson and J. W. Haught, *Bull. West Va. Univ. Sci. Assoc.*, 1930, **2**, No. 4, 8; *A.*, 700; E. M. Emmert, *J. Assoc. Off. Agric. Chem.*, 1931, **14**, 386; *A.*, 1142; U. Boklund, *Biochem. Z.*, 1931, **233**, 478; *A.*, 1024; J. Lindner and F. Hernler, *Mikrochem.*, Emich Festschr., 1930, 191; *A.*, 1930, 1543; M. Nicloux, *Compt. rend. Soc. Biol.*, 1929, **101**, 182; *A.*, 186.

[15] J. C. Olsen, G. E. Ferguson, V. J. Sabetta, and L. Scheflan, *Ind. Eng. Chem. (Anal.)*, 1931, **3**, 189; *A.*, 700.

Hydrogen is readily absorbed by a silver permanganate reagent;[16] two manometric methods for the determination of hydrogen peroxide are described.[17] Work on helium is continued.[18]

Continuing his bromo-iodometric investigations, J. H. van der Meulen[19] describes methods (*a*) of determining iodate and bromate together, (*b*) of determining iodate, bromate, and chlorate together, (*c*) of oxidising bromide to bromate with hypochlorite, (*d*) of destroying excess of hypochlorite by boiling with sodium formate or a little osmic acid, (*e*) of reducing chlorate to chloride by arsenite, with osmate as catalyst, (*f*) or by ferrous sulphate in presence of hydrobromic acid and osmate as catalyst. Other papers in the halogen group deal with chlorides,[20] bromides,[21] iodine and iodides,[22] and fluorides.[23]

Some conditions for determining nitrates by phenoldisulphonic acid are laid down.[24] Nitrates are quantitatively reduced electro-

[16] F. Hein and W. Daniel, *Chem. Fabr.*, 1931, 381; *A.*, 1256.

[17] A. Fujita and T. Kodama, *Biochem. Z.*, 1931, **232**, 15; *A.*, 699.

[18] F. Paneth and W. D. Urry, *Mikrochem.*, Emich Festschr., 1930, 233; *A.*, 1930, 1543; *Z. physikal. Chem.*, 1931, **152**, 110, 127; *A.*, 327; *ibid.*, Bodenstein Festband, 1931, 145; *A.*, 1258; V. A. Sokolov, *Neft. Khoz.*, 1930, **19**, 292; *A.*, 452.

[19] *Chem. Weekblad*, 1930, **27**, (*a*) p. 578; (*b*) p. 618; 1931, **28**, (*c*) p. 82; (*d*) p. 238; (*e*) p. 258; (*f*) p. 348; *A.*, 1930, 1542; 1931, 55, 325, 699, 699, 811.

[20] A. V. Frost, *Trans. Inst. Pure Chem. Reagents*, 1929, No. 300, 187; *A.*, 1930, 1541; G. G. Longinescu and T. J. Pirtea, *Bul. Chim. Soc. Română Stiin.*, 1928, **31**, 77; *A.*, 585; I. E. Orlov, *Z. anal. Chem.*, 1931, **84**, 185; *A.*, 811; A. B. Keys, *J.*, 1931, 2440; *A.*, 1257; V. N. Kolitscheva and R. V. Teis, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 1957; *A.*, 450: O. Tomíček and O. Pročke, *Coll. Czech. Chem. Comm.*, 1931, **3**, 116; *A.*, 450; H. Ruoss, *Z. anal. Chem.*, 1930, **81**, 385; *A.*, 1930, 1541; Cousin and Dufour, *J. Pharm. Chim.*, 1930, [viii], **12**, 439; *A.*, 55.

[21] Z. Szabó, *Z. anal. Chem.*, 1931, **84**, 24; *A.*, 811; B. S. Evans, *Analyst*, 1931, **56**, 590; *B.*, 1009; M. Bobtelsky and R. Rosovskaja-Rossienskaja, *Z. anorg. Chem.*, 1931, **199**, 283; *A.*, 1257.

[22] R. W. Teiss, *Z. anal. Chem.*, 1930, **82**, 116; *A.*, 1930, 1542; H. Ditz, *Z. anorg. Chem.*, 1930, **194**, 147; *A.*, 185; F. L. Hahn, *ibid.*, 1931, **195**, 75; *A.*, 325; H. A. Liebhafsky, *J. Amer. Chem. Soc.*, 1931, **53**, 165; *A.*, 325; R. E. Remington, J. F. McClendon, and H. von Kolnitz, *ibid.*, p. 1245; *A.*, 699; P. Fleury and J. Courtois, *Bull. Soc. chim.*, 1931, [iv], **49**, 860; *A.*, 1023.

[23] A. Kurtenacker and W. Jurenka, *Z. anal. Chem.*, 1930, **82**, 210; *A.*, 1930, 1542; M. Karasiński, *Bull. Acad. Polonaise*, 1931, [*A*], 143; *A.*, 1257; P. Mougnaud, *Compt. rend.*, 1931, **192**, 1733; *A.*, 1023; A. V. Frost, *Trans. Inst. Pure Chem. Reagents*, 1931, **10**, 53; *A.*, 925; G. Batchelder and V. W. Meloche, *J. Amer. Chem. Soc.*, 1931, **53**, 2131; *A.*, 925; H. Ginsberg, *Chem.-Ztg.*, 1931, **55**, 608.

[24] B. A. Skopintzev, *J. Appl. Chem. Russia*, 1930, **3**, 747; *A.*, 326; *Z. anal. Chem.*, 1931, **85**, 244; *A.*, 1257.

lytically at a copper or nickel cathode.[25] A phosphate buffer of p_H 7·4 is recommended for the recovery of free ammonia from ammonium chloride and sulphate solutions;[26] oxidation of ammonia to nitrogen by bromine is quantitative in solutions of p_H 7·5—9·5.[27] A volumetric method for very small quantities of ammonia, especially in waters, is described.[28] Alkali azides are titrated with silver nitrate in presence of potassium chromate;[29] hydrazine and semicarbazide may be determined by oxidation with potassium iodate,[30] and nitrites colorimetrically with rivanol;[31] the reaction between nitrite and iodide has been examined.[32]

Several papers deal with the determination of phosphoric acid;[33] and methods are given for the removal of phosphate ions from solution in analysis.[34] Hypophosphites and arsenites are determined by reaction with mercuric chloride.[35] Potassium permanganate is applied colorimetrically as a reagent for lower oxides in phosphoric oxide.[36]

Modifications have been introduced into certain methods of determining persulphate to increase their accuracy;[37] a scheme is proposed for mixtures of Caro's acid, persulphate, and hydrogen peroxide.[38] Further observations are made on volumetric methods for sulphates,[39] and on the precipitation as barium sulphate in the

[25] L. Szebellédy and B. M. Schall, *Z. anal. Chem.*, 1931, **86**, 127; *A.*, 1257.

[26] M. S. Nicholls and M. E. Foote, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 311; *A.*, 1023.

[27] B. Levy, *Z. anal. Chem.*, 1931, **84**, 98; M. Tschepelevetzky, S. Posdniakova, and R. Fein, *ibid.*, p. 106; *A.*, 1024.

[28] S. K. Hagen, *ibid.*, **83**, 164; *A.*, 586.

[29] A. Majrich, *Chem. Obzor*, 1930, **5**, 3; *A.*, 186.

[30] V. Hovorka, *Coll. Czech. Chem. Comm.*, 1931, **3**, 285; *A.*, 925.

[31] W. M. Rubel, *Z. Unters. Lebensm.*, 1930, **60**, 588; *A.*, 586.

[32] C. A. Abeledo and I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1931, **53**, 2893; *A.*, 1142.

[33] A. del Campo, *Anal. Fís. Quím.*, 1930, **28**, 1153; *A.*, 55; H. T. Bucherer and F. W. Meier, *Z. anal. Chem.*, 1931, **85**, 331; *A.*, 1258; H. Thurnwald and A. A. Benedetti-Pichler, *ibid.*, **86**, 41; *A.*, 1258; S. L. Lieboff, *J. Lab. Clin. Med.*, 1931, **16**, 495; *A.*, 1258; R. Biazzo, *Ann. Chim. Appl.*, 1931, **21**, 21, 75; *A.*, 452; *ibid.*, p. 105; *A.*, 700; G. Denigès, *Bull. Soc. Pharm. Bordeaux*, 1930, **68**, 1; *A.*, 927; M. Ishibashi, Chikashige Anniv. Vol., 1930, 1; *A.*, 586; A. von Endrédy, *Z. anorg. Chem.*, 1930, **194**, 239; *A.*, 186.

[34] A. Kešans, *Latvij. Univ. Raksti*, 1929, **1**, 65; *A.*, 1930, 1543; J. Bougault and E. Cattelain, *J. Pharm. Chim.*, 1931, [viii], **14**, 97; *A.*, 1142.

[35] A. Ionesco-Matiu and (Mme.) A. Popesco, *ibid.*, **13**, 12; *A.*, 326.

[36] J. W. Smith, *J.*, 1931, 528; *A.*, 587.

[37] A. Kurtenacker and H. Kubina, *Z. anal. Chem.*, 1931, **83**, 14; *A.*, 452.

[38] K. Gleu, *Z. anorg. Chem.*, 1931, **195**, 61; *A.*, 326.

[39] I. M. Kolthoff and E. B. Sandell, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 115; *A.*, 451; Chatron, *J. Pharm. Chim.*, 1931, [viii], **13**, 244; *A.*, 586; M. Dominikiewicz, *Bull. Trav. Dep. Chim. Inst. Hyg. État.* (*Poland*), 1930, **31**, No. 1, 3; *A.*, 185.

presence of lead salts[40] and of various chromium compounds.[41] A buffered ammonia solution is added prior to the oxidation of thiocyanate by iodine.[42]

With the view of application to the analysis of natural selenides, methods have been devised for determination of copper[43] and silver selenites[44] in the presence of the corresponding selenides. For the rapid precipitation of selenium, large quantities of hydrazine hydrochloride are recommended.[45] Both selenious and silicic acids may be determined colorimetrically by reaction with pyrrole although the colour fades rather rapidly.[46] A nitric–perchloric acid mixture is used for the determination of silica in vegetable substances.[47]

Organic Analysis.

Qualitative.—For purposes of identification of various phenols there are described the corresponding phenoxyacetic acids[48] and 3 : 5-dinitrobenzoates;[49] of fatty acids, the *p*-bromophenacyl esters[50] and alkylbenziminazoles;[51] of alcohols, the *p*-nitrophenylurethanes;[52] of alcohols and phenols, the *p*-xenylcarbamates;[53] of primary and secondary alcohols and certain phenols, the hydantoin-3-acetates;[54] of carbonyl compounds, the 2 : 4-dinitrophenylhydrazones;[55] of halides, as 3 : 5-dinitrobenzoates[56]

[40] B. Tézak, *Arhiv Hemiju*, 1930, **4**, 78; *A.*, 1930, 1542.

[41] E. A. Nikitina and A. V. Babajeva, *Trans. Inst. Pure. Chem. Reagents*, 1931, **10**, 20; *A.*, 925.

[42] H. A. Pagel and H. J. Koch, *J. Amer. Chem. Soc.*, 1931, **53**, 1774; *A.*, 811.

[43] W. Geilmann and F. W. Wrigge, *Z. anorg. Chem.*, 1931, **197**, 353; *A.*, 813.

[44] F. W. Wrigge, *ibid.*, p. 369; *A.*, 813.

[45] E. Benesch and E. Erdheim, *Chem.-Ztg.*, 1930, **54**, 954; *A.*, 185; K. Wagenmann and H. Triebel, *Metall u. Erz*, 1930, **27**, 231; *A.*, 186.

[46] R. Berg and M. Teitelbaum, *Mikrochem.*, Emich Festschr., 1930, 23; *A.*, 1930, 1546.

[47] L. Lematte, G. Boinot, E. Kahane, and (Mme.) M. Kahane, *Compt. rend.*, 1931, **192**, 1459; *A.*, 926.

[48] C. F. Koelsch, *J. Amer. Chem. Soc.*, 1931, **53**, 304; *A.*, 345.

[49] M. Phillips and G. L. Keenan, *ibid.*, p. 1924; *A.*, 837.

[50] S. G. Powell, *ibid.*, p. 1172; *A.*, 621.

[51] R. Seka and R. H. Müller, *Monatsh.*, 1931, **57**, 97; *A.*, 600.

[52] R. L. Schriner and R. F. B. Cox, *J. Amer. Chem. Soc.*, 1931, **53**, 1601; *A.*, 709.

[53] G. T. Morgan and A. E. J. Pettet, *J.*, 1931, 1124; *A.*, 834.

[54] R. Locquin, V. Cerchez, and A. A. Policard, *Bull. Soc. chim.*, 1931, [iv], **49**, 595, 600, 602, 607; *A.*, 966.

[55] O. L. Brady, *J.*, 1931, 756; *A.*, 937.

[56] C. L. Tseng and E. J. H. Chu, *Nat. Centr. Univ. Sci. Rep.*, [*A*], 1930, **1**, 9; *A.*, 504.

and as anilides;[57] of ethers, as alkyl 3 : 5-dinitrobenzoates or bromo-derivatives.[58]

The sensitivity of various methods, old and new, for the detection of carbon disulphide has been ascertained.[59] The blue coloration produced with iodine and lanthanous salts is a delicate test for acetic acid; benzoic acid and homologues of acetic acid react similarly or inhibitatively.[60] Colour reactions are described for certain higher aliphatic acids,[61] β-naphthol,[62] phenols generally,[63] and *o*-dihydroxyphenols in particular,[64] for certain diamino- and nitroamino-diphenyl sulphides,[65] glyoxaline derivatives and tyrosine,[66] thiolglyoxalines,[67] morphine,[68] adrenaline,[69] salicylic acid and salol,[70] phenyl *o*-acetoxybenzoate,[71] tannin, gallic acid, and pyrogallol,[72] quinones,[73] aromatic amines [74] and the toluidines in particular,[75] ephedrine,[76] cystine,[77] eugenol and clove oil,[78] carbo-

[57] A. M. Schwartz and J. R. Johnson, *J. Amer. Chem. Soc.*, 1931, **53,** 1063; *A.*, 597.

[58] H. W. Underwood, jun., O. L. Baril, and G. C. Toone, *ibid.*, 1930, **52,** 4087; *A.*, 1930, 1554.

[59] F. Feigl and K. Weisselberg, *Z. anal. Chem.*, 1931, **83,** 93; *A.*, 638; S. L. Malowan, *ibid.*, **84,** 406; *A.*, 1078.

[60] E. Tschirch, *Oesterr. Chem.-Ztg.*, 1931, **34,** 38; *A.*, 601; D. Krüger and E. Tschirch, *Mikrochem.*, 1930, **8,** 337; *A.*, 335.

[61] L. Ekkert, *Pharm. Zentr.*, 1931, **72,** 228; *A.*, 710.

[62] G. de Haas, *Pharm. Weekblad*, 1931, **68,** 29; *A.*, 347.

[63] C. D. Leake, *Proc. Soc. Exp. Biol. Med.*, 1930, **28,** 148; *A.*, 856; V. E. Levine, *J. Amer. Pharm. Assoc.*, 1931, **20,** 537; *A.*, 972; M. François and (Mlle.) L. Seguin, *Bull. Soc. chim.*, 1931, [iv], **49,** 680; *A.*, 972; L. Rosenthaler, *Pharm. Ztg.*, 1931, **76,** 888; *A.*, 1174.

[64] J. H. Quastel, *Analyst*, 1931, **56,** 311; *A.*, 856.

[65] H. H. Hodgson and W. Rosenberg, *J. Soc. Dyers Col.*, 1930, **46,** 267; *A.*, 84.

[66] E. Gebauer-Fülnegg, *Z. physiol. Chem.*, 1930, **191,** 222; *A.*, 1930, 1605; J. A. Sánchez, *Semana méd.*, 1930, I, 1579; *A.*, 108.

[67] G. Hunter, *J.*, 1930, 2343; *A.*, 1930, 1596.

[68] F. Bamford, *Analyst*, 1931, **56,** 586; *A.*, 1312; L. Rossi, *Anal. Farm. Bioquím.*, 1930, **1,** 106; *A.*, 1319.

[69] B. Azzolini, *Boll. chim.-farm.*, 1931, **70,** 665; *A.*, 1318.

[70] L. Ekkert, *Pharm. Zentr.*, 1930, **71,** 744; *A.*, 88.

[71] H. Szancer, *ibid.*, 1931, **72,** 68; *A.*, 351.

[72] M. N. A. de Celsi and S. A. Celsi, *Anal. Farm. Bioquím.*, 1931, **2,** 56; *A.*, 1174.

[73] R. Craven, *J.*, 1931, 1605; *A.*, 972.

[74] I. de Paolini, *Atti R. Accad. Sci. Torino*, 1930, **65,** 201; *A.*, 638.

[75] W. H. Patterson, *J.*, 1930, 2401; *A.*, 1930, 1605.

[76] W. H. Hartung, F. Crossley, and J. C. Munch, *J. Pharm. Chim.*, 1931, [viii], **13,** 474; *A.*, 724; J. Sivadjian, *ibid.*, 1930, **12,** 266; *A.*, 1930, 1460; *idem*, *ibid.*, 1931, **14,** 61; *A.*, 1079.

[77] J. A. Sánchez, *Semana méd.*, 1930, II, 31; *A.*, 1930, 1563.

[78] H. Szancer, *Bull. Sci. pharmacol.*, 1929, **36,** 611; *A.*, 1930, 1605.

hydrates and related compounds,[79] benzene, naphthalene, etc., *p*-benzoquinone, and quinoline,[80] and the nitro-group.[81]

The Scott–Wilson reagent for acetone and acetaldehyde can be made specific for the former.[82] Micro-crystallographic data are given for mesaconic acid and certain of its derivatives; [83] the fluorescent properties of umbelliferone enable its formation from malic acid and resorcinol to serve as specific tests for these substances.[84] Differentiation of cyclic monophenols and monoamines from polyphenols and polyamines is effected by means of phosphotungstic and phosphomolybdic reagents.[85] Triketohydrindene hydrate is not a trustworthy reagent for the products of protein hydrolysis.[86] The action of iodine and bromine on unsaturated barbituric acid derivatives in bicarbonate solution is described; [87] " veronalides " are diagnosed micro-crystalloscopically.[88]

Alkaloids are classified in nine groups according to their sensitivity towards precipitating agents, their solubility in water and the basic strength of the free alkaloids; [89] a tabulation is made of the microchemical reactions of 78 alkaloids with a number of reagents.[90] Limiting concentrations for the micro-precipitation of alkaloids by sodium alizarinsulphonate are recorded; [91] sulphonic acids of other anthraquinone derivatives form crystalline precipitates with organic bases.[92] Microchemical methods are described for the detection of strychnine,[93] *l*-ephedrine and ephetonine,[94] cytisine,[95] echinopsine,[96] nicotine,[97] colchicine,[98] piperine,[99] and choline.[1] The formation

[79] J. S. Hepburn and M. Lazarchick, *Amer. J. Pharm.*, 1930, **102**, 560; *A.*, 69.
[80] L. Ekkert, *Pharm. Zentr.*, 1931, **72**, 51; *A.*, 375.
[81] P. K. Bose, *Analyst*, 1931, **56**, 504; *A.*, 1148.
[82] L. Kline, *Arhiv Hemiju*, 1931, **5**, 212; *A.*, 1273.
[83] H. H. Mottern and G. L. Keenan, *J. Amer. Chem. Soc.*, 1931, **53**, 2347; A., 1036.
[84] L. Columbier, *Ann. Falsif.*, 1931, **24**, 89; *A.*, 698.
[85] A. Marenzi, *Anal. Farm. Bioquím.*, 1930, **1**, 99; *A.*, 375.
[86] H. Gardner, *Lancet*, 1930, ii, 525; *A.*, 972.
[87] J. Bougault and J. Guillon, *Compt. rend.*, 1931, **193**, 463; *A.*, 1308.
[88] G. Denigès, *Mikrochem.*, 1931, **9**, 316; *A.*, 966.
[89] C. C. Fulton, *J. Assoc. Off. Agric. Chem.*, 1930, **13**, 491; *A.*, 243.
[90] J. F. H. Amelink, *Pharm. Weekblad*, 1931, **68**, 159, 211, 221; *A.*, 504.
[91] L. Rosenthaler, *Apoth.-Ztg.*, 1930, **45**, 638; *A.*, 375.
[92] W. Zimmermann, *Z. physiol. Chem.*, 1930, **188**, 180; **189**, 155; **192**, 124; *A.*, 1930, 941, 1170, 1605.
[93] V. D. Gnesin, *Farm. Zhur.*, 1930, 293; *A.*, 1079.
[94] L. Rosenthaler, *Z. anal. Chem.*, 1931, **86**, 61; *A.*, 1319.
[95] G. Klein and E. Farkass, *Oesterr. Bot. Z.*, 1930, **79**, 107; *A.*, 243.
[96] G. Klein and F. Schusta, *ibid.*, p. 231; *A.*, 639.
[97] G. Klein and E. Herndlhofer, *ibid.*, **76**, 222; *A.*, 639.
[98] G. Klein and G. Pollauf, *ibid.*, 1929, **78**, 251; *A.*, 778.
[99] G. Klein and M. Krisch, *ibid.*, p. 257; *A.*, 778.
[1] G. Klein and A. Zeller, *ibid.*, **79**, 40; A., 778.

of the substance responsible for the thalleioquinine reaction is retarded by a decrease in p_H.[2]

Reactions of choline and lecithin,[3] creatine and creatinine,[4] alanine,[5] antipyrine and pyramidone,[6] narceine,[7] dulcine,[8] and mezcaline [9] are given. Sodium nitroprusside gives colour reactions with a variety of organic compounds.[10] Iodine tetrachloride is used for the microchemical identification of a number of alkaloids ; [11] *p*-toluenesulphonic acid is suggested as condensing agent for the detection of alcohols by the odour of their esters, and *iso*propyl alcohol can be recognised in presence of ethyl alcohol by its reaction with protocatechualdehyde.[12]

An account is given of the application of micro-sublimation methods to the identification of small quantities of materials,[13] and an apparatus described for the extraction of benzoic and other aromatic acids.[14]

Quantitative.—Sulphur is eliminated in direct combustions for carbon by a plug of asbestos upon which red lead has been sublimed.[15] The extent to which combustion tubes and the materials used in organic elementary analysis yield water on ignition has been investigated ; [16] advantages are claimed for copper tubes in combustions.[17] Investigations on the elementary analysis of organic compounds may be reviewed under the following heads: carbon and hydrogen,[18] nitrogen,[19]

[2] J. Eisenbrand, *Arch. Pharm.*, 1931, **269**, 65 ; *A.*, 639.

[3] J. A. Sánchez, *Semana méd.*, 1930, I, 1416 ; *A.*, 75.

[4] *Idem, ibid.*, II, 616 ; *A.*, 246.

[5] *Idem, ibid.*, 1931, I, 651 ; *A.*, 1042.

[6] M. Ribère, *J. Pharm. Chim.*, 1930 [viii], **12**, 444 ; *A.*, 99.

[7] J. A. Sanchez, *Anal. Farm. Bioquim.*, 1931, **2**, 68 ; *A.*, 1174.

[8] *Idem, ibid.*, p. 63 ; *A.*, 1174.

[9] L. Rosenthaler, *Pharm. Ztg.*, 1931, **76**, 653 ; *A.*, 1318.

[10] T. Pavolini, *Boll. chim.-farm.*, 1930, **69**, 713 ; *A.*, 1930, 1605.

[11] L. Rosenthaler, *Pharm. Ztg.*, 1931, **76**, 524 ; *A.*, 857.

[12] *Idem, ibid.*, 775 ; *A.*, 971.

[13] A. Chalmeta, *Anal. Fis. Quim.*, 1930, **28**, 1407 ; *A.*, 246.

[14] A. N. Leather, *Analyst*, 1931, **56**, 299 ; *A.*, 856.

[15] W. H. Blatchley, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 13 ; *A.*, 503.

[16] J. Lindner, *Ber.*, 1931, **64**, [*B*], 1560 ; *A.*, 1078.

[17] N. Klatschin, *Z. anal. Chem.*, 1930, **82**, 133 ; *A.*, 1930, 1604.

[18] H. Lieb and H. G. Kraineck, *Mikrochem.*, 1931, **9**, 367 ; *A.*, 971 ; J. B. Niederl and J. R. Meadow, *ibid.*, p. 350 ; *A.*, 971 ; A. Verdino, *ibid.*, p. 123 ; *A.*, 638 ; A. Friedrich, *ibid.*, p. 20 ; *A.*, 374 ; M. Furter, *ibid.*, p. 27 ; *A.*, 374 ; F. Hernler, *ibid.*, 1930, Emich Festschr., 148 ; *A.*, 107 ; E. P. Griffing and C. L. Alsberg, *J. Amer. Chem. Soc.*, 1931, **53**, 1037 ; *A.*, 638 ; E. Stansfield and J. W. Sutherland, *Canadian J. Res.*, 1930, **3**, 318 ; *A.*, 1930, 1604.

[19] W. J. Saschek, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 198 ; *A.*, 700 ; N. M. Stover and R. B. Sandin., *ibid.*, p. 240 ; *A.*, 1024 ; W. F. Allen, *ibid.*, p. 239 ; *A.*, 1024 ; O. R. Trautz and J. B. Niederl, *ibid.*, p. 151 ; *A.*, 752 ; J. J. Rutgers, *Compt. rend.*, 1931, **193**, 51 ; *A.*, 1024 ; J. Schmidt and W. Maier, *Ber.*, 1931,

halogens,[20] and phosphorus.[21] A volumetric method of determining methoxyl and ethoxyl groups is described [22] which may also be used on the micro-scale; [23] modifications are made in the micro-Zeisel process to render it applicable to polymethoxy-compounds.[24] The Fuchs–Hunter–Edwards method for determining carboxyl groups is adapted for micro-work.[25] The use of benzyl-alcoholic alkali is recommended for the determination of acetyl groups in substituted acetamides.[26] Some errors in analytical bromination have been investigated, and a process is detailed for the measurement of organic unsaturation.[27]

Oxidation of small amounts of ethyl alcohol with chromic acid gives results comparable with those obtained by the specific gravity method; [28] a modified micro-Zeisel process has been applied to this alcohol.[29] Reaction with ethyl formate and ethoxide to give sodium formate serves to prepare anhydrous alcohol and to determine the water content of alcohol.[30] An account is given of the use of Ilosvay's reagent for the determination of traces of acetylene.[31] Reaction of formaldehyde or hexamethylenetetramine with methone should be effected in neutral solution.[32] Modifications of existing methods are made for the determination of solid saturated [33] and

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64, [*B*], 778; *A.*, 752; F. Govaert, *Natuurwetensch. Tijds.*, 1931, **13,** 127; *A.*, 856; *idem, Mikrochem.*, 1931, **9,** 338; *A.*, 971; *idem, Ann. Chim. analyt.*, 1931, [ii], **13,** 229; *A.*, 1142; J. C. Harral, *Analyst*, 1931, **56,** 527; *A.*, 1174; M. Weizmann, J. Yofe, and B. Kirzon, *Z. physiol. Chem.*, 1930, **192,** 70; *A.*, 1930, 1604; A. C. Anderson and B. N. Jensen, *Z. anal. Chem.*, 1931, **83,** 114; *A.*, 638; O. R. Trautz, *Mikrochem.*, 1931, **9,** 300; *A.*, 971.

[20] B. Bobrański, *Rocz. Chem.*, 1931, **11,** 301; *Z. anal. Chem.*, 1931, **84,** 225; *A.*, 856; F. Schulz, *Coll. Czech. Chem. Comm.*, 1931, **3,** 281; *A.*, 945.

[21] W. C. Davies and D. R. Davies, *J.*, 1931, 1207; *A.*, 856.

[22] F. Vieböck and A. Schwappach, *Ber.*, 1930, **63,** [*B*], 2818; *A.*, 107.

[23] F. Vieböck and C. Brecher, *ibid.*, p. 3207; *A.*, 246.

[24] (Miss) G. M. Ware, *Mikrochem.*, 1930, **8,** 352; *A.*, 374.

[25] S. Tsurumi and Y. Sasaki, *Sci. Rep. Tôhoku Imp. Univ.*, 1930, **19,** 681; *A.*, 504.

[26] S. Sabetay and J. Sivadjian, *J. Pharm. Chim.*, 1931, [viii], **13,** 530; *A.*, 856.

[27] H. M. Buckwalter and E. C. Wagner, *J. Amer. Chem. Soc.*, 1930, **52,** 5241; *A.*, 193.

[28] S. G. Liversedge, *Analyst*, 1931, **56,** 595; *A.*, 1267; M. Nicloux, *Compt. rend.*, 1931, **192,** 985; *A.*, 752; *idem, Bull. Soc. Chim. biol.*, 1931, **13,** 857; *A.*, 1327.

[29] J. B. Niederl and B. Whitman, *Z. anal. Chem.*, 1931, **86,** 65; *A.*, 1318.

[30] F. Adickes, W. Brunnert, and O. Lücker, *Ber.*, 1930, **63,** [*B*], 2753; *A.*, 61.

[31] W. Riese, *Z. angew. Chem.*, 1931, **44,** 701; *A.*, 1318; see also E. Czakó, *ibid.*, p. 388; *A.*, 819; and E. Pietsch and A. Kotovski, *ibid.*, p. 388; *A.*, 819.

[32] V. Ionescu and C. Bodea, *Bull. Soc. chim.*, 1930, [iv], **47,** 1408; *A.*, 335.

[33] T. P. Hilditch and J. Priestman, *Analyst*, 1931, **56,** 354; *A.*, 935.

of solid unsaturated [34] fatty acids, and for Okey's method for cholesterol.[35] Methods involving the use of iodine monochloride or bromide are found to be unsuitable for the determination of the iodine value of cholesterol owing to substitution; Kaufmann's method is preferred, with that of Rosenmund and Kuhnhenn as second choice.[36] A quantitative separation of saturated and unsaturated sterols depends on the fact that cholesterol dibromide is not precipitated by digitonin.[37] Work on the oxidation of sugars by iodine in presence of alkali,[38] by ferricyanide,[39] and by cupro-potassium carbonate solutions [40] has been extended. A colorimetric method with acid molybdate is applied to lævulose in presence of certain other sugars; [41] some factors governing the fermentation of polysaccharides are discussed.[42]

The humic acid content of dilute solutions is ascertained by permanganate oxidation under prescribed conditions.[43] The composition of the phospho- and silico-tungstates of choline and allied bases has been recorded.[44] The p_H at which phosphotungstate precipitates of certain bases appear depends largely on the constitution of the base; [45] reaction between nicotine and silicotungstic acid, applied volumetrically, does not appear to be stoicheiometric.[46] Values of p_H at the end-point of the neutralisation of alkaloid bases have been deduced, and suitable indicators for the titration selected; [47] colorimetric methods are described for mor-

[34] L. V. Cocks, B. C. Christian, and G. Harding, *Analyst*, 1931, **56**, 368; *A.*, 935.

[35] M. Yasuda, *J. Biol. Chem.*, 1931, **92**, 303; *A.*, 1318; M. E. Turner, *ibid.*, p. 495; *A.*, 1174; see R. Okey, *ibid.*, 1930, **88**, 367; *A.*, 1930, 1303.

[36] H. Werner, *Z. Unters. Lebensm.*, 1931, **61**, 321; *A.*, 1318.

[37] R. Schönheimer, *Z. physiol. Chem.*, 1930, **192**, 77; *A.*, 1930, 1616.

[38] G. M. Kline and S. F. Acree, *Ind. Eng. Chem. (Anal.)*, 1930, **2**, 413; *A.*, 1930, 1560; *Bur. Stand. J. Res.*, 1930, **5**, 1063; *A.*, 199.

[39] A. C. Hulme and R. Narain, *Biochem. J.*, 1931, **25**, 1051; *A.*, 1274; E. M. Widdowson, *ibid.*, p. 863; *A.*, 1102; O. Lehmann, *Planta*, 1931, **13**, 575; *A.*, 1038.

[40] H. A. Schuette and J. N. Terrill, *J. Amer. Chem. Soc.*, 1930, **52**, 4960; *A.*, 199.

[41] H. Bredereck, *Ber.*, 1931, **64**, [*B*], 1730; *A.*, 1039.

[42] E. Schmidt, M. Atterer, and H. Schnegg, *Cellulosechem.*, 1931, **12**, 235; *A.*, 1038.

[43] D. J. W. Kreulen, *Brennstoff-Chem.*, 1931, **12**, 265; *A.*, 1148.

[44] L. Lematte, G. Boinot, E. Kahane, and (Mme.) M. Kahane, *J. Pharm. Chim.*, 1931, [viii], **13**, 371; *A.*, 606; *Compt. rend.*, 1930, **191**, 1130; *A.*, 338.

[45] R. A. Peters, *Biochem. J.*, 1930, **24**, 1852; *A.*, 374.

[46] B. Kasansky, *Z. anal. Chem.*, 1931, **83**, 107; *A.*, 639.

[47] E. B. R. Prideaux and F. T. Winfield, *Analyst*, 1930, **55**, 561; *A.*, 246; compare also F. Reimers, *Dansk Tidsskr. Farm.*, 1931, **5**, 42; *A.*, 752.

phine, heroine, and physostigmine,[48] cryogenin,[49] tryptophan,[50] strychnine, emetine, cinchonine, and quinine,[51] cystine[52] and cysteine.[53] Serine in hot alkaline solution gives ammonia, glycine, alanine, and oxalic and lactic acids.[54] The precipitate formed from choline with excess of gold chloride is stable to concentration and can be washed with water.[55] In dilute alcohol–ether solution novocaine, but not cocaine, is precipitated by picric acid;[56] a mixture of chloroform and *iso*propyl alcohol is recommended for the extraction of morphine from its aqueous suspension.[57] Conditions are prescribed for the quantitative saponification of the lactone group in narcotine and santonin.[58] An iodo-gasometric method for determining cysteine (or, after reduction, cystine) is described.[59]

Pyramidone is quantitatively precipitated by an excess of mercuric chloride; antipyrine is precipitated also, but not quantitatively.[60] Mercurimetric methods have applied to citrates, salicylates, and benzoates.[61] Verley and Bolsing's method has been applied to the determination of the hydroxyl group in castor oil and various phenols.[62] Determination of phenylhydrazine gasometrically is applied to the evaluation of the carbonyl group of ketones and aldehydes;[63] the method involving formation of iodoform from the COMe group in acetone can be extended to many ketones containing this group.[64]

Conditions for the alkalimetric titration of 2 : 4-dinitrophenol

48 L. David, *Pharm. Ztg.*, 1931, **76**, 706; *A.*, 972.

49 G. Denigès, *Bull. Pharm. Soc. Bordeaux*, 1930, **68**, 49, 51; *A.*, 504.

50 T. Ruemele, *Z. anal. Chem.*, 1931, **84**, 81; *A.*, 1079.

51 C. A. Rojahn and R. Seifert, *Arch. Pharm.*, 1930, **268**, 499; *A.*, 1930, 1605.

52 M. X. Sullivan, *U.S. Pub. Health Rep. Suppl.*, 1929, No. 78; M. X. Sullivan and D. B. Jones, *ibid.*, No. 82; M. X. Sullivan and W. C. Hess, *ibid.*, No. 86; *A.*, 1930, 1604.

53 *Idem, ibid.*, Reprint No. 1450; *A.*, 831.

54 F. S. Daft and R. D. Coghill, *J. Biol. Chem.*, 1931, **90**, 341; *A.*, 638.

55 L. Pincusson and E. von Heyden, *Biochem. Z.*, 1931, **234**, 484; *A.*, 829.

56 F. Weiss, *Apoth.-Ztg.*, 1930, **45**, 724; *A.*, 375.

57 H. Baggesgaard-Rasmussen and S. A. Schou, *Arch. Pharm.*, 1930, **268**, 673; *A.*, 371.

58 A. P. Snesarov, *J. Chem. Ind. Russia*, 1931, **8**, 161; *A.*, 752.

59 H. D. Baernstein, *J. Biol. Chem.*, 1930, **89**, 124; *A.*, 108.

60 R. Machtou, *J. Pharm. Chim.*, 1931, [viii], **13**, 329; *A.*, 639.

61 A. Ionescu-Matiu and (Mme.) Popesco, *ibid.*, **14**, 54; *A.*, 1079.

62 S. Marks and R. S. Morrell, *Analyst*, 1931, **56**, 428; *A.*, 1035; Huppmann, *Pharm. Ztg.*, 1931, **76**, 113; *A.*, 752.

63 S. Marks and R. S. Morrell, *Analyst*, 1931, **56**, 508; *A.*, 1149.

64 V. Cuculescu, *Bul. Fac. Stiinte Cernauti*, 1928, **2**, 143; *A.*, 752.

are prescribed; [65] cuprammonium sulphate precipitates picric acid as a picrate which may be weighed.[66] Trinitrotoluene, but not trinitroxylene, is converted by *p*-nitrosodimethylaniline in presence of pyridine and a trace of iodine into the azomethine compound which is weighed.[67] Reduction with titanous chloride is applied on a micro-scale to various aromatic nitro-compounds.[68] Examination has been made of the methods of analysing cresols.[69]

Physical Methods.

There has been a discussion on titration in Wood's light.[70] Calcium oxalate is considered unsuitable for nephelometry,[71] which has been applied to the determination of sulphates.[72]

Methods involving extinction coefficients have been applied to benzene in alcohol [73] and to thiocyanate.[74] Photoelectric methods are used for dilute solutions generally [75] and for certain hydroxy-acids.[76] The copper salts of the amino-acids show characteristic absorption curves.[77] Partition constants for pairs of fatty acids between ether and water have been ascertained; [78] camphor affects the surface tension of a dilute alcohol solution proportionately.[79] An " isopyknoscopic " method can be used for ascertaining the concentration of solutions of pure compounds.[80] Radiometric microanalysis is used in sulphide determinations and oxidimetry.[81] Atmospheric ozone is determined by an optical method; [82] the

[65] A. Suchier, *Z. anal. Chem.*, 1931, **85**, 434; *A.*, 1318.

[66] M. François and (Mlle.) L. Seguin, *Ann. Falsif.*, 1930, **23**, 481; *A.*, 107.

[67] S. Secareanu, *Ber.*, 1931, **64**, [*B*], 834; *A.*, 752.

[68] S. Maruyama, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1931, **16**, 196; *A.*, 1318.

[69] P. Dumont, *J. Pharm. Belg.*, 1930, **12**, 1, 21, 41, 65, 87; *A.*, 375.

[70] A. G. Nasini and P. de Cori, *Atti III Cong. Naz. Chim.*, 1929, 668; *A.*, 924.

[71] A. I. Polinkovski, *Trans. State Inst. Test. Building Mat.*, 1929, No. 27, 11; *A.*, 1259.

[72] Chatron, *J. Pharm. Chim.*, 1931, [viii], **13**, 321; *A.*, 586; S. W. Parr and W. D. Staley, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 66; *A.*, 451.

[73] G. Gróh and E. Faltin, *Magyar Chem. Fol.*, 1930, **36**, 156; *A.*, 638.

[74] C. Urbach, *Biochem. Z.*, 1931, **237**, 189; *A.*, 1257.

[75] M. Matsui and T. Noda, *J. Soc. Chem. Ind. Japan*, 1930, **33**, 517; *A.*, 325.

[76] A. S. Williams, R. H. Müller, and J. B. Niederl, *Mikrochem.*, 1931, **9**, 269; *A.*, 935.

[77] H. Ley and B. Arends, *Z. physiol. Chem.*, 1930, **192**, 131; *A.*, 1930, 1604.

[78] C. H. Werkman, *Iowa State Coll. J. Sci.*, 1930, **4**, 459; *A.*, 374.

[79] M. L. Nichols and A. Stubblefield, *Z. anal. Chem.*, 1931, **86**, 30; *A.*, 1318.

[80] A. Del Campo, C. Nogareda, and M. G. de Celis, *Anal. Fis. Quim.*, 1931, **29**, 386; *A.*, 924.

[81] R. Ehrenberg, *Mikrochem.*, Emich Festschr., 1930, 120; *A.*, 1930, 1542.

[82] A. I. Duninowski, *Compt. rend.*, 1930, **191**, 859; *A.*, 55.

pressure at which phosphorus starts to glow is governed by the proportion of hydrocarbon in the air or oxygen.[83] Mixtures may be analysed by monochromatic transmission.[84] A method for reducing the errors of colorimetric determinations is recorded.[85]

X-Ray methods have been applied quantitatively to certain rare-earth mixtures,[86] to copper–silver and –zinc alloys,[87] to certain other binary alloys,[88] and qualitatively to distinguish between magnesite and dolomites.[89] Spectro-analytical methods are described for the determination of traces of mercury,[90] of strontium in calcium,[91] of traces of nickel and chromium,[92] of binary alloys,[93] of various gases,[94] of metals in solution,[95] and qualitatively for traces of impurities in metals; [96] a means of increasing the accuracy of quantitative emission spectral analysis is indicated.[97]

Electrolytic.—Small electrodes are described for qualitative microelectrolysis.[98] Several papers deal with the electro-analytical separation of copper.[99] Lead is deposited free from antimony from alkaline tartrate solutions under certain conditions.[1]

The series of polaro-graphic studies with the dropping-mercury cathode have been continued.[2]

[83] J. Tausz and H. Görlacher, *Z. anal. Chem.*, 1931, **83**, 81; *A.*, 587.

[84] M. Barnard and P. McMichael, *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 363; *A.*, 1930, 1541.

[85] F. F. Hahn and R. Klockmann, *Z. angew. Chem.*, 1930, **43**, 993; *A.*, 54.

[86] P. Günther, A. Kotovski, and H. Lehl, *Z. anorg. Chem.*, 1931, **200**, 287; *A.*, 1261.

[87] H. Terrey and E. G. V. Barrett, *J. Physical Chem.*, 1931, **35**, 1156; *A.*, 702.

[88] G. R. Fonda and G. B. Collins, *J. Amer. Chem. Soc.*, 1931, **53**, 113; *A.*, 328.

[89] F. Halla, *Monatsh.*, 1931, **57**, 1; *A.*, 453.

[90] W. Gerlach and E. Schweitzer, *Z. anorg. Chem.*, 1931, **195**, 255; *A.*, 328.

[91] K. Ruthardt, *ibid.*, p. 15; *A.*, 327.

[92] A. J. de A. Gouveia, *Rev. Chim. pura appl.*, 1930, **5**, 41; *A.*, 1143.

[93] G. Guzzoni, *Atti III Cong. Naz. Chim.*, 1929, 636; *A.*, 924.

[94] B. de la Roche, *Bull. Soc. chim.*, 1930, [iv], **47**, 1326; *A.*, 185.

[95] F. Twyman and C. S. Hitchen, *Proc. Roy. Soc.*, 1931, [*A*], **133**, 72; *A.*, 1260.

[96] L. Amey, *Compt. rend.*, 1930, **191**, 1049; *A.*, 187; H. E. Redeker and P. A. Leighton, *J. Amer. Chem. Soc.*, 1930, **52**, 4169; *A.*, 1930, 1546.

[97] G. Scheibe, C. F. Linström, and O. Schoettler, *Z. angew. Chem.*, 1931, **44**, 145; *A.*, 924.

[98] H. J. Brenneis, *Mikrochem.*, 1931, **9**, 385; *A.*, 924.

[99] H. Hölemann, *Z. anal. Chem.*, 1930, **81**, 161; *A.*, 57; *idem, ibid.*, **82**, 273; *A.*, 187; T. L. Kelly and J. J. Molloy, *J. Amer. Chem. Soc.*, 1931, **53**, 1337; *A.*, 702; C. Zbinden, *Bull. Soc. Chim. biol.*, 1931, **13**, 35; *A.*, 701; N. H. Furman, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 217; *A.*, 701.

[1] E. M. Collin and H. J. S. Sand, *Analyst*, 1931, **56**, 90; *A.*, 588.

[2] J. Heyrovský and V. Nejedlý, *Coll. Czech. Chem. Comm.*, 1931, **3**, 126; *A.*, 451; K. Suchý, *ibid.*, p. 354; *A.*, 1025; J. Prajzler, *ibid.*, p. 406; *A.*, 1261; J. Heyrovský, *Arhiv Hemiju*, 1931, **5**, 162; *A.*, 1257.

Potentiometric.—Methods are described for the titration of lead with chromate,[3] of silver iodide,[4] of silver, cupric, and mercuric ions with cobalticyanide,[5] of iridium,[6] of bivalent platinum,[7] of uranium,[8] of zinc,[9] of ferric and dichromate ions with uranous sulphate,[10] of ferrocyanide and nitrite mutually,[11] of Caro's acid and hydrogen peroxide,[12] of carbonate,[13] of phosphoric acid,[14] of cystine and cysteine,[15] of certain drugs [16] and alkaloids,[17] of piperidine in mixture with pyridine and its homologues,[18] and of amino-nitrogen.[19] The point of inflexion on the titration curve of zinc chloride with sodium hydroxide occurs before two equivalents of the alkali have been added.[20]

The value of two solid electrodes in cases involving titrations with ferrocyanide and with silver nitrate,[21] and some factors concerned in differential titration [22] have been studied.

Conductometric.—The titration of sulphate and barium,[23] of molybdenum, tungsten, and thallium,[24] the influence of small amounts of carbonic acid on the titration of acids and bases,[25]

[3] R. W. Gelbach and K. G. Compton, *Ind. Eng. Chem.* (*Anal.*), 1930, **2,** 397; *A.*, 1930, 1545.

[4] E. Lange and R. Berger, *Z. Elektrochem.*, 1930, **36,** 980; *A.*, 186.

[5] L. Czaporowski and J. Wierciński, *Rocz. Chem.*, 1931, **11,** 95; *A.*, 588.

[6] S. C. Woo and D. M. Yost, *J. Amer. Chem. Soc.*, 1931, **53,** 884; *A.*, 590.

[7] O. Stelling, *Svensk Kem. Tidskr.*, 1931, **43,** 130; *A.*, 814.

[8] D. T. Ewing and (Mrs.) M. Wilson, *J. Amer. Chem. Soc.*, 1931, **53,** 2105; *A.*, 927; N. H. Furman and I. C. Schoonover, *ibid.*, p. 2561; *A.*, 1026; M. A. Luyckx, *Bull. Soc. chim. Belg.*, 1931, **40,** 269; *A.*, 1026.

[9] E. Brennecke, *Z. anal. Chem.*, 1931, **86,** 175; *A.*, 1260.

[10] E. H. Ducloux, *Rev. Fac. Cienc. quim., La Plata*, 1930, **7,** II, 97; *A.*, 1025.

[11] J. V. Romón, *Anal. Fís. Quím.*, 1930, **28,** 1045; *A.*, 1930, 1542.

[12] E. Müller and G. Holder, *Z. anal. Chem.*, 1931, **84,** 410; *A.*, 1023.

[13] A. Ringbom, *ibid.*, p. 161; *A.*, 812.

[14] A. Sanfourche, *Compt. rend.*, 1931, **192,** 1225; *A.*, 812.

[15] K. Yamazaki, *J. Biochem. Japan*, 1930, **12,** 207; *A.*, 374.

[16] L. Maricq, *Bull. Soc. chim. Belg.*, 1931, **40,** 361; *A.*, 1318.

[17] *Idem, ibid.*, **39,** 496; *A.*, 375; M. L. Holt and L. Kahlenberg, *J. Amer. Pharm. Assoc.*, 1931, **20,** 11; *A.*, 375.

[18] A. Travers and Franquin, *Compt. rend.*, 1930, **191,** 1340; *A.*, 375.

[19] J. Roche and (Mme.) A. Roche, *Bull. Soc. Chim. biol.*, 1931, **13,** 835; *A.*, 1318.

[20] M. Prytz, *Z. anorg. Chem.*, 1931, **200,** 133; *A.*, 1260.

[21] J. A. Atanasiu and A. J. Velculesco, *Z. anal. Chem.*, 1931, **85,** 120; *A.*, 1260.

[22] D. A. MacInnes and I. A. Cowperthwaite, *J. Amer. Chem. Soc.*, 1931, **53,** 555; *A.*, 450.

[23] I. M. Kolthoff and T. Kameda, *Ind. Eng. Chem.* (*Anal.*), 1931, **3,** 129; *A.*, 699.

[24] G. Jander, *Z. angew. Chem.*, 1930, **43,** 930; *A.*, 1930, 1548.

[25] W. Poethke, *Z. anal. Chem.*, 1931, **86,** 45; *A.*, 1256.

and the titration of organic acids and bases in benzene [26] have been studied. For binary mixtures of formic, acetic, propionic, and *n*-butyric acids, the antilog of $\kappa \times 10^3$ is a linear function of the composition.[27] On account of ready oxidation in alkaline solution preventing the use of ordinary indicators in the determination of the acetyl group in acetylated derivatives of polyhydric phenols, the conductometric method is utilised.[28]

J. J. Fox.
B. A. Ellis.

[26] V. K. LaMer and H. C. Downes, *J. Amer. Chem. Soc.*, 1931, **53**, 888; *A.*, 584.

[27] E. I. Fulmer, E. E. Moore, and R. L. Foster, *J. Physical Chem.*, 1931, **35**, 1227; *A.*, 1078.

[28] C. Torres, A. S. Capuchino, and L. Socias, *Anal. Fis. Quím.*, 1930, **28**, 694; *A.*, 1930, 1605.

BIOCHEMISTRY.

UNQUESTIONABLY the most striking achievements in biochemistry during the past year are to be seen in the noteworthy advances in our knowledge of the fat-soluble vitamins and of their precursors. In particular it is the pleasing task of the Reporter to review the steps which have led to the isolation for the first time of a crystalline substance which has every claim to be regarded as a vitamin in a state of purity. The culmination of much patient work carried out principally in this country, in Germany, and in Holland has resulted in the identification of the antirachitic vitamin D with a crystalline isomeride of ergosterol to which Dr. Bourdillon and his co-workers have given the name of "calciferol."

In the section devoted to plant biochemistry particular attention has been given this year to matters relating to, or arising from, the mineral nutrition of plants. To make this portion of the Report as complete as possible, reference has been made to many publications which appeared prior to the year under review, but have not hitherto been noted in these Reports.

Vitamin D and Ergosterol.

It will be evident from the review of the position given in the Report of last year,[1] that the methods and results there described provided a reasonable basis for the expectation that the workers in the Medical Research Council's laboratory would before long have the pure vitamin in their hands. Events have fully justified this expectation. In the course of the year under review there were described, in addition to the crystalline material already mentioned in the Report of last year,[2] three other crystalline preparations of very high antirachitic potency. The main properties of these are summarised in Table I.

TABLE I.

Preparation.	M. p.	Rotation.	Max. U. V. absorption.	Analysis.
Angus *et al.*	123—125°	$[\alpha]_{5461}$ +260° in alcohol	270 mμ	$C_{27}H_{42}O$
Reerink and van Wijk	115—117°	$[\alpha]_D$ +100° in ether	—	$C_{27}H_{42}O$
Windaus	122—123°	$[\alpha]_{5461}$ +169° in acetone	265—270 mμ	$C_{27}H_{42}O$

The first-mentioned of these preparations, to which the name "calciferol" was first given, was described by T. C. Angus, F. A.

[1] *Ann. Reports*, 1930, **27**, 277. [2] *Ibid.*, p. 278.

Askew, R. B. Bourdillon, H. M. Bruce, R. K. Callow, C. Fischmann, J. St. L. Philpot, and T. A. Webster.[3] It is essentially the crystalline preparation described last year, obtained in larger quantity and in a state of greater purity by improvements in the technique of preparation and isolation. The second preparation is that of E. H. Reerink and A. van Wijk,[4] whilst the third was obtained by A. Windaus.[5] All three preparations proved to have approximately the same antirachitic activity ranging from 20,000 to 25,000 international units [6] per milligram of substance. The absorption spectra were similar, and all three substances might lay claim to be regarded as isomerides of ergosterol, as will be seen from the analytical data quoted. None the less, the specific rotations of the three preparations varied considerably, and it seemed evident that they could not be regarded as being identical or homogeneous. On the other hand, there was strong presumptive evidence that the antirachitic activity of calciferol was an inherent property of the crystals and was not due to traces of an active contaminant, but the possible presence of an inactive impurity could not be excluded. It is to be noted that the distillation method used by Angus *et al.* for the isolation of the crystalline substance involved the subjection of the irradiation product to temperatures of the order of 150°. On the other hand, Windaus obtained his crystalline material with the avoidance of high temperatures. He treated irradiated ergosterol, freed from unchanged sterol, with maleic anhydride in ether at room

[3] *Proc. Roy. Soc.*, 1931, *B*, **108**, 340; *A.*, 881.

[4] *Biochem. J.*, 1931, **25**, 1001; *A.*, 1197.

[5] *Proc. Roy. Soc.*, 1931, *B*, **108**, 568; *A.*, 1098.

[6] The international unit of antirachitic potency was defined at the League of Nations Conference in June, 1931. It is the " vitamin D activity of 1 mg. of the International Standard Solution of irradiated ergosterol." The standard solution is made by dissolving a particular sample of irradiated ergosterol in olive-oil, so that 1 gram of the oil contains 0·1 milligram of the irradiated material. 1 Milligram of the oily solution therefore contains 1/10,000 milligram of the mixed products of irradiation, and this, by definition, contains 1 international unit of vitamin D activity. It was fixed at this value, since experiments showed that 1 unit *per diem*, given to a rachitic rat, was about the dose required to produce healing in ten days, the total amount administered being, therefore, ten units. The international unit has the same value as the unit previously adopted by the Medical Research Council, which body has been mainly responsible for the adoption of the present International Standard. It is probable that in the near future the unit will be more conveniently re-defined in terms of pure calciferol. If this is done, it is likely to be on a strictly comparative basis so that the unit will remain unchanged in value, but will be referred to a given weight of a standard sample of pure calciferol.

The information embodied in this footnote has been given to the Reporter by Sir H. H. Dale, C.B.E., F.R.S., of the Medical Research Council, London.

temperature. The portions which had reacted with the anhydride were then removed with dilute potash solution, and the remaining product readily crystallised on evaporation of the solvent. Recrystallisation was easily effected from various solvents. The Reerink and van Wijk preparation was obtained by methods permitting of the irradiation and all subsequent extraction and crystallisation procedures being carried out in a vacuum at the ordinary temperature.

With these facts in mind the Medical Research Council workers turned their attention to the possible presence in their crystalline material of the products of thermal decomposition of the irradiation products. They were able to show that, when the active crystalline material was heated at 180°, it was transformed into an inactive crystalline isomeride of ergosterol which had a remarkably high dextrorotation, and to which they gave the name " pyrocalciferol." It therefore seemed highly probable that calciferol obtained by distillation might be contaminated with pyrocalciferol and that such contamination might well account for its high dextrorotation.

A considerable advance was foreshadowed when R. K. Callow [7] referred to the preparation of a crystalline ester—the 3 : 5-dinitrobenzoate—of calciferol from which the active crystalline material could be regenerated by hydrolysis. Evidence was obtained of the separation of the ester into two components, and it was suggested that the distilled product was a mixture, or a molecular compound, of pyrocalciferol and a substance with a higher antirachitic activity than any product obtained up to that time. F. A. Askew, H. M. Bruce, R. K. Callow, J. St. L. Philpot, and T. A. Webster [8] later published results fully confirming this hypothesis. The active crystalline material was treated with 3 : 5-dinitrobenzoyl chloride in pyridine, and the product separated by fractional crystallisation into two esters, both of which were repeatedly recrystallised. Calciferyl 3 : 5-dinitrobenzoate, m. p. 147—149°, yields on hydrolysis calciferol, m. p. 114·5—117°, having $[\alpha]_{5461}^{20°} + 122{\cdot}5°$, $[\alpha]_{D}^{20°} + 102{\cdot}5°$ in alcohol, and $[\alpha]_{5461}^{20°} + 98{\cdot}5°$, $[\alpha]_{D}^{20°} + 81°$ in acetone. Its solution in alcohol has an intense absorption band with a maximum at 265 mμ and it possesses an antirachitic activity of 40,500 international units per milligram, which is approximately twice that of any previous preparation containing vitamin D. Pyrocalciferyl 3 : 5-dinitrobenzoate, m. p. 167·5—169·5°, on hydrolysis yields

[7] " Chemistry at the Centenary Meeting of the British Association," Heffer and Son, Cambridge, 1932. (The Reporter is indebted to Mr. J. Davidson Pratt of the Association of British Chemical Manufacturers for a copy of the proofs of this forthcoming publication.)

[8] *Nature*, 1931, **128**, 758.

pyrocalciferol, m. p. 93—95°, having $[\alpha]_{5461}^{20^\circ} + 624^\circ$, $[\alpha]_{D}^{20^\circ} + 502^\circ$ in alcohol. The maximum absorption is at 284 mμ. Pyrocalciferol has no antirachitic activity. Both calciferol and pyrocalciferol have been shown on analysis to have the same empirical formula as ergosterol.

In addition to pyrocalciferol there is present in the crystalline material obtained by Dr. Bourdillon and his co-workers [9] another irradiation product, which has been called " sterol X." This substance has been isolated in a crystalline condition (see Table II). Its colour reactions with trichloroacetic acid and with mercuric acetate in nitric acid [10] indicate the presence of a $\Delta^{1:2}$ (or $\Delta^{1:13}$)-linkage, which is also present in ergosterol but not in calciferol or pyrocalciferol. As in the case of the two last-mentioned sterols, " sterol X " forms a crystalline 3 : 5-dinitrobenzoate by means of which it has been separated from the corresponding ester of calciferol.

The supposition that calciferol is a direct product of the irradiation of ergosterol is confirmed by the isolation of its 3 : 5-dinitrobenzoate from the undistilled, crude irradiation product. The ester and the parent calciferol thus obtained are identical with those obtained from the distilled material, and the yield is such that the greater part of the antirachitic activity of the crude resin can be accounted for by the calciferol actually isolated as the ester. Sterol X is also found in the undistilled irradiation product.

It will be realised from the foregoing that the substance first provisionally called " calciferol " proved to be a mixture, or solid solution, of two molecular compounds of true calciferol (or pure vitamin D) with pyrocalciferol and with sterol X. None the less the name calciferol is retained (at least by the British workers) for the vitamin, since it is pointed out [11] that the term vitamin D is inconvenient when referring to esters and other derivatives of the compound, and the adoption of a new name would tend to confusion.

While these developments were occurring in this country a paper by A. Windaus, A. Lüttringhaus, and M. Deppe [12] carried the German work a stage further. The crystalline product already described was further characterised and termed " vitamin D_1." In an addendum to this paper by O. Linsert there was mentioned a

[9] F. A. Askew, R. B. Bourdillon, H. M. Bruce, R. K. Callow, J. St. L. Philpot, and T. A. Webster, *Proc. Roy. Soc.*, 1932, *B*, **109**, 488. (The Reporter is indebted to Sir H. H. Dale, C.B.E., F.R.S., Director-in-Chief of The Medical Research Council's laboratory, for a proof copy of this paper.)

[10] O. Rosenheim, *Biochem. J.*, 1929, **23**, 47; *A.*, 1929, 359; O. Rosenheim and R. K. Callow, *ibid.*, 1931, **25**, 74; *A.*, 529.

[11] F. A. Askew, R. B. Bourdillon, *et al.*, *loc. cit.*

[12] *Annalen*, 1931, **489**, 252; *A.*, 1464.

second crystalline substance which was referred to as " vitamin D_2." Its quoted optical rotation and melting point were very similar to those of calciferol, sufficiently so to suggest identity to the British workers. At first Windaus regarded D_1 and D_2 as independent antirachitic substances of approximately equal activity. Later, as a result of interchange of materials and results with the British workers, Windaus and his colleagues, making use of the dinitrobenzoyl esters, were able to fractionate D_1 into D_2 and an inactive substance which is identical with sterol X, and for which the German workers have suggested the name " lumisterin." [13] It has further been established that the antirachitic activity of D_2 is twice that of the D_1 crystalline material, and therefore equal to that of pure calciferol. There can therefore remain little doubt that the calciferol of the British workers and the vitamin D_2 of the German workers are identical and approximately pure specimens of the antirachitic vitamin.[14] In Table II a summary is given of the salient properties of the known transformation products and of their derivatives arising from ergosterol in the course of the formation of vitamin D.

There remains to be considered the crystalline material isolated by Reerink and van Wijk. The experiments of these workers led them to the conclusion that their active crystalline material (which they called substance L) was formed in one step from ergosterol when the latter was subjected to radiations not shorter than 284 mμ in wave-length. This is inferred from the fact that the rotation of the ergosterol during irradiation shows a linear dependence on its degree of transformation as deduced from a determination of the unchanged ergosterol by the digitonin method. Whilst the transformation of ergosterol into vitamin D must be regarded as a simple unimolecular rearrangement, it is now quite clear that other transformation products are formed concurrently, and it seems very probable that substance L is a mixture of calciferol and one or more of the inactive irradiation products.

Criteria of Purity of Calciferol.—In any other class of chemical compounds the evidence of purity and homogeneity discussed in the foregoing paragraphs would be accepted as convincing. In the sterol group, however, the occurrence of association compounds and of solid solutions is very frequent, and this renders difficult the attainment of certainty regarding the purity of a new compound. It is at the present time impossible to secure complete proof that the activity of calciferol is not due to small quantities of an intensely

[13] A. Lüttringhaus, *Chem.-Ztg.*, 1931, **55**, 936. Presumably the English equivalent " lumisterol " will be adopted in this country.—J. P.

[14] A. Windaus and A. Lüttringhaus, *Z. physiol. Chem.*, 1931, **203**, 75 (addendum); F. A. Askew, R. B. Bourdillon, *et al.*, *loc. cit.*

TABLE II.

Properties of Calciferol, and Allied Compounds, and their Esters.

Substance.	Melting point.	$[\alpha]_{5461}^{20°}$. Ethyl alcohol.	$[\alpha]_{5461}^{20°}$. Acetone.	$[\alpha]_{D}^{20°}$. Ethyl alcohol.	$[\alpha]_{D}^{20°}$. Acetone.	Maximum absorption. ε.	Maximum absorption. γ, mμ.	Antirachitic activity (international units per mg.).
Sterols.								
1. Purified calciferol	114·5—117°	+122·5°	+ 98·5°	+102·5°	+ 81°	48	265	40,483 (mean)
2. Vitamin D_2 (*a*)	114 —115	—	—	—	+ 85	47	265	—
,, (*b*)	110·5—113·5	+120	—	—	—	43	263	44,600
3. Vitamin D_1 (*c*)	124 —125	+174	—	+141	—	32	268	—
,, (*d*)	124 —127	+176	—	—	+136·3	32	268	23,700
4. Pyrocalciferol	93 — 95	+624	—	+502	—	{16, 27, 26}	{296, 284, 274}	—
5. Sterol X	116·5—118·5	+220	—	+176	—	21	280	—
6. Crystalline distillation products (*e*)	123 —125	+260	—	—	—	34	270	20,000 (mean)
Crystalline distillation products (*f*)	119 —123 to 121 —125	+220 to 325	—	—	—	33	270	20,000 (mean)
7. Calciferol–pyrocalciferol, 1 : 1 mixture.	120 —122·5	+374	—	—	—	35 (observed)	272	—
						36 (calculated)	273	—
3 : 5-*Dinitrobenzoates.*		In benzene.						
1. Of calciferol	147 —149	+69·5	+105	—	—	—	—	—
2. Of vitamin D_2 (*g*)	145 —147	+70·5	+105·5	—	—	—	—	—
3. Of pyrocalciferol	167·5—169·5	+250	—	—	—	—	—	—
4. Of sterol X	139·6—141·5	+ 24	—	—	—	—	—	—

(*a*) Prepared by Windaus, Lüttringhaus, and Deppe (*loc. cit.*).
(*b*) Prepared by Windaus (not quite pure).
(*c*) Prepared by Askew, Bourdillon, *et al.* (*loc. cit.*).
(*d*) Prepared by Windaus.
(*e*) Prepared by Askew *et al.* (*loc. cit.*).
(*f*) Later specimens.
(*g*) Prepared by Windaus.

active contaminant, but this is rendered most improbable by the relative ease with which closely allied sterols (pyrocalciferol and sterol X) can be separated from it without perceptible antirachitic activity. Moreover, the different preparations of calciferol show very little variation in physical properties, whether prepared from the irradiation products of ergosterol by direct esterification, or after removal of contaminants, or by distillation and subsequent esterification. Due allowance being made for the errors in the biological method of assay, a reasonable constancy in the antirachitic activity may also be claimed. Finally, calciferol yields crystalline esters which, on recrystallisation and hydrolysis, give back the original sterol with unchanged physical and biological properties.

It is to be anticipated that the nature of the active group or groups in vitamin D should soon be elucidated. The results already outlined point to the presence of three double bonds, as in ergosterol, but one at least of these bonds is in a position different from that of the parent sterol. Windaus [15] accepts as proved the view that the antirachitic activity is specifically associated with the presence of the hydroxyl group. In support of this he points out that, if the highly active crude irradiation product is carefully treated with phenyl *iso*cyanate, a derivative completely lacking in antirachitic activity is obtained. But if this derivative is warmed with alcoholic potash, it is reconverted into a highly active material. Alternatively, ergosterol phenylurethane may be irradiated. It is found to undergo some change, but it does not acquire antirachitic activity. If, however, the irradiation product is hydrolysed, a highly active substance is produced.

Toxic Effects of Excess of Calciferol.—In recent years many observations have been made concerning the toxic effects of excessive administration of irradiated ergosterol and of other preparations containing vitamin D. Various aspects of the resulting pathological manifestations have been attributed to the vitamin itself and to its accompanying contaminants, for instance, the "calcinosis" factor.[16] In view of the advances of the past year there is little doubt that a clearer insight into such problems will be gained, and if the calcinosis factor, and similar hypothetical substances, are real entities their differentiation from the true vitamin should be relatively simple. In the meantime attention is directed to some preliminary results recorded by Askew *et al.*[17] Tests carried out on mice show that the minimal toxic dose of calciferol is of the order 0·1 mg., of crude calciferol 0·2 mg., and of a preparation of Windaus's D_1 0·2 mg. The ratio of the toxic dose (in mice) to the curative

[15] *Loc. cit.* [16] *Ann. Reports*, 1930, **27**, 279.
[17] F. A. Askew, R. B. Bourdillon, *et al.*, *loc. cit.*

dose (in rats) is therefore about 4000/1. These results are not claimed as final, but they support the view that the toxicity is an inherent property of the pure vitamin and is not due to a contaminant. A. Windaus, P. Busse, and G. Weidlich [18] and L. J. Harris and J. R. M. Innes [19] have arrived at a similar conclusion. The last-mentioned workers have furnished evidence which substantiates the theory that vitamin D exerts its toxic action by raising the blood calcium or phosphate. It is shown that this increase is associated with an increased net absorption from the gut, which is of special importance in hypervitaminosis with diets rich in calcium, but also that the shaft of the bone may provide an important additional source in certain circumstances, for instance, on low calcium diets and with a larger excess of vitamin D.

Vitamin A and Carotene.

In the Reports for the past two years [20] there have been reviewed the results of numerous investigations of the possible relationship of the hydrocarbon carotene to vitamin A. Interest in this field has continued to develop, and the newly acquired biological interest of the hydrocarbon has stimulated the organic chemist to provide much interesting and welcome information concerning its chemical nature. On this purely chemical side the investigations of Professors P. Karrer and R. Kuhn are especially noteworthy.

The Carotenoids.—Karrer states that there are ten basic types of carotenoid pigments.[21] These are found in plants and in animals both in the free form and, in some cases, as esters. Three carotenoids are carboxylic acids, namely, crocetin, $C_{20}H_{24}O_4$, bixin, $C_{25}H_{30}O_4$, and azaffrin, and these alone are stable in the presence of oxygen. Three carotenoids are hydrocarbons, namely, lycopene, $C_{40}H_{56}$, and the two isomeric α- and β-forms of carotene, $C_{40}H_{56}$. The remaining members of the group contain two or more hydroxyl groups. These are the α- and β-xanthophylls, $C_{40}H_{56}O_2$; zeaxanthin, $C_{40}H_{56}O_2$, violaxanthin, $C_{40}H_{56}O_4$, and capsanthin, $C_{34}H_{48}O_3$ or $C_{35}H_{50}O_3$.

Carotenes.—Of these natural pigments, only the α- and β-carotenes are capable of restoring growth in animals which have been deprived of vitamin A. Partial reduction of α- and β-carotenes yields α- and β-dihydrocarotenes,[22] which have not yet been crystallised. These both contain the β-ionone ring with its double bond. It has been

[18] *Z. physiol. Chem.*, 1931, **202**, 246.
[19] *Biochem. J.*, 1931, **25**, 367; *A.*, 659.
[20] *Ann. Reports*, 1929, **26**, 245; 1930, **27**, 276.
[21] "Chemistry at the Centenary Meeting of the British Association," Heffer and Son, Cambridge, 1932.
[22] J. H. C. Smith, *J. Biol. Chem.*, 1931, **90**, 597; *A.*, 491.

claimed that these dihydrocarotenes can serve as a source of vitamin A,[23] but J. C. Drummond [24] states that this is not so when precautions are taken to free the hydrogenated product from all traces of unchanged carotene. It has likewise been claimed [25] that di-iodo-carotene is biologically active, but this appears to be so only in as far as carotene is regenerated from it in the body. Kuhn [26] and Karrer [27] and their respective co-workers have made a study of the separation of the α- and β-carotenes. Kuhn states that α-carotene melts at 175—176° and has $[\alpha]_{Cd}$ + 365° in benzene, whilst the β-form melts at 181—182° and is optically inactive. The ratio of α-carotene to β-carotene varies considerably in different plants and many carotenes are found to consist exclusively of the β-form. In Table III there are reproduced some of Kuhn's figures regarding the rotatory power and α-carotene content of different preparations.

TABLE III.

Material.	$[\alpha]^{20°}_{Cd}$.	α-Carotene, %.
Palm oil	+ 120—170°	30—50
Horse chestnut leaves	90	25
Carrots	30—70	10—20
Sorb apples	50	15
Stinging nettles, Grass, Spinach, Capsicum fruits	0	0

The carotene prepared from the *corpora lutea* of cows consists exclusively of the β-form, the explanation for which is found in the occurrence of the β-form alone in grass. A mutual interconversion of the α- and β-forms does not seem to occur *in vivo*. A third form of the hydrocarbon, called *iso*carotene,[28] is known, but this does not occur as a natural product, nor does it give rise to vitamin A in the animal body.[29] It is formed when β-carotene is precipitated with an excess of iodine and the resulting iodide decomposed with sodium thiosulphate or mercury. It contains 13 double bonds like the open-chain lycopene, that is, two more than natural carotene.

The formula of carotene has already been discussed in these

[23] P. Karrer, H. von Euler, H. Hellström, and M. Rydbom, *Svensk Kem. Tidskr.*, 1931, **43**, 105; H. von Euler, P. Karrer, H. Hellström, and M. Rydbom, *Helv. Chim. Acta*, 1931, **14**, 839; *A.*, 1097.

[24] "Chemistry at the Centenary Meeting of the British Association," Heffer and Son, Cambridge, 1932.

[25] *Ann. Reports*, 1929, **26**, 246.

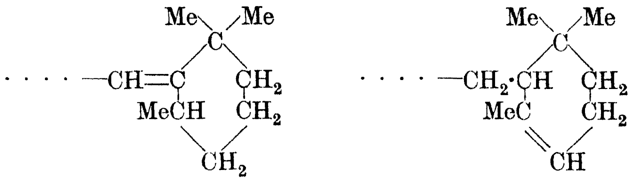
[26] R. Kuhn and E. Lederer, *Naturwiss.*, 1931, **19**, 306; *Ber.*, 1931, **64**, [*B*], 1349.

[27] P. Karrer, A. Helfenstein, H. Wehrli, B. Pieper, and R. Morf, *Helv. Chim. Acta*, 1931, **14**, 614; *A.*, 733.

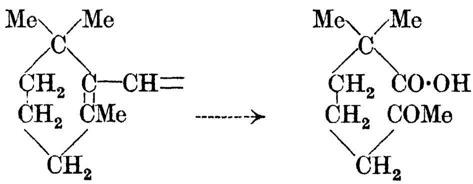
[28] R. Kuhn and E. Lederer, *loc. cit.*

[29] R. Kuhn and R. Brockmann, *Ber.*, 1931, **64**, [*B*], 1859; *A.*, 1097.

Reports [30] and it will suffice to state here that the formula originally suggested is retained for β-carotene, whilst two alternative ring structures, each with an asymmetric carbon atom, are tentatively advanced for α-carotene, the optically active form :—

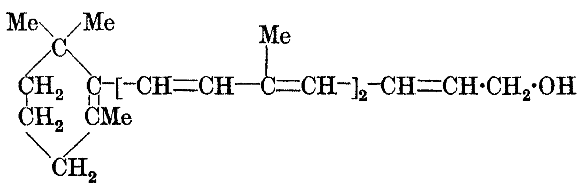


Carotene and Vitamin A.—The structural relationship of carotene to vitamin A remains to be elucidated. H. R. Bruins, J. Overhoff, and L. K. Wolff [31] have measured the diffusion constants of carotene and vitamin A in xylene and from these the ratio of the molecular weights of the two substances has been calculated. A molecular weight of about 330 is deduced for the vitamin. The molecular weight of carotene is 536, so that a simple direct relationship between the hydrocarbon and the vitamin appears to be excluded. P. Karrer, R. Morf, and K. Schöpp,[32] from the ozonisation of the purest available preparations of vitamin A, have obtained geronic acid, which is also obtained by a similar treatment of carotene :



Geronic acid.

The inference is that vitamin A contains in its molecule the same ring as β-ionone and β-carotene.[33] A substance of the following structure, which might be obtained by oxidative disruption of a molecule of carotene, has been tentatively discussed by Karrer as a working hypothesis in considering the structure of the vitamin:



[30] *Ann. Reports*, 1930, **27**, 167. [31] *Biochem. J.*, 1931, **25**, 430; *A.*, 771.
[32] *Helv. Chim. Acta*, 1931, **14**, 1036; *A.*, 1463.
[33] See also R. Pummerer, L. Rebmann, and W. Reindel, *Ber.*, 1931, **64**, [*B*], 492; *A.*, 491.

As has already been stated, both the α- and the β-form of carotene are biologically active. H. von Euler [34] finds that the β-form shows some advantage in this respect over the α-form, but it is clear that both forms show a biological activity which must be independent of the asymmetric carbon atom. Certain results quoted by R. Kuhn [35] show that the β-form has a decided advantage when small doses are given and when the feeding period is short. With larger amounts of the carotenes and longer feeding periods the difference becomes smaller, but does not disappear, as will be seen from the results given in Table IV.

There is general agreement that the transformation of carotene into the vitamin takes place in the liver, although von Euler does not exclude the possible participation of the bone marrow in the process. Indeed, H. S. Olcott and D. C. McCann [36] claim to have

TABLE IV.

No. of rats.	Mg. Carotene per day.	Feeding period in days.	Blue units per g. liver using $SbCl_3$ test (av. values).
8	0·45 α	6	8
7	1·00 α	12	190
8	1·00 α	19	290
6	0·45 β	6	80
8	1·00 β	12	400
8	1·00 β	19	825

effected the transformation *in vitro* by incubating the hydrocarbon with fresh liver tissue or with an aqueous extract of liver. The agent responsible for the change is destroyed by heat and is therefore regarded as an enzyme, to which the name *carotenase* is provisionally assigned. H. von Euler,[37] on the other hand, has not been able to obtain clear evidence of such a transformation *in vitro,* and B. Ahmad [38] states that it does not occur.

T. Moore [39] was one of the first workers in the vitamin field to obtain direct evidence of the accumulation of vitamin A in the livers of animals fed on carotene. Moore [40] now finds that the concentration of the vitamin in the " storage " fats of the body as a result of such feeding is only about 1/100,000 that of the concentration in the liver, whilst other tissues give very weak or negative reactions

[34] H. von Euler, P. Karrer, H. Hellström, and M. Rydbom, *loc. cit.*

[35] " Chemistry at the Centenary Meeting of the British Association," Heffer and Son, Cambridge, 1932.

[36] *J. Biol. Chem.*, 1931, **94**, 185.

[37] " Chemistry at the Centenary Meeting of the British Association," Heffer and Son, Cambridge, 1932.

[38] *Biochem. J.*, 1931, **25**, 1195; *A.*, 1196.

[39] *Ann. Reports*, 1929, **26**, 247; 1930, **27**, 276.

[40] *Biochem. J.*, 1931, **25**, 275; *A.*, 529.

for the vitamin (von Euler and his co-workers state that bone marrow is a rich source of the vitamin). In another communication Moore[41] points out that the vitamin A reserves of the average mammal per gram of liver tissue are of much the same order as those of the average fish, the superiority of the extracted mammal-liver oil being largely due to the much smaller amount of fat present. The use of the mammal, however, affords the very great advantage that the diet can be arranged so as to ensure that the vitamin A content of the liver will approach its maximum. A suitable animal, such as a rat or a pig, may be " fattened up " on a diet rich in carotene or preformed vitamin A and so used as a " factory " for the concentration of the vitamin. Moore's experiments along these lines, on animals fed with red palm oil, have yielded highly concentrated preparations of the vitamin with a minimal daily rat dose of 0·001 mg. The degree of concentration attained in these experiments will be appreciated from Table V. In this the " blue units " quoted, in reference to the antimony trichloride colour test, are not necessarily the same as those used by other workers. Thus the

TABLE V.

Material.	Blue units per mg.	Approx. minimal rat dose (mg.).
Butter fat	0.02	20
Cod-liver oil	1	1
Jersey cow-liver oil	100	—
Cod-liver oil concentrates	400	0·005
Liver oil of rat fed on Red Palm oil	600	—
Concentrate from liver oil of rats fed with R.P.O.	2000	0·001
Concentrate from pig fed with R.P.O.	2600	—

figure 2,600 blue units per mg. corresponds to a blue value of 40,000 calculated on the cod-liver oil scale of Drummond and Hilditch. Moore points out that, as far as can be judged, the biological activity of the best concentrates is not more than 2 or 3 times that of carotene, and that this slight superiority might be visualised as being due to the inefficient conversion of the extremely unstable carotene, or possibly to the cutting down of the molecule during conversion. The latter possibility accords with the views of Karrer[42] and of Bruins, Overhoff, and Wolff[43] already discussed.

Spectrographic Behaviour of Vitamin A.—In previous Reports reference has been made to the spectrographic test for vitamin A introduced by R. A. Morton and I. M. Heilbron.[44] These investig-

[41] " Chemistry at the Centenary Meeting of the British Association," Heffer and Son, Cambridge, 1932.

[42] *Loc. cit.* [43] *Loc. cit.*

[44] *Ann. Reports*, 1928, **25**, 268; 1929, **26**, 248.

ators, together with their collaborators,[45] have made a systematic study of materials containing vitamin A with respect to the antimony trichloride colour reaction and the ultra-violet absorption spectrum. It must be borne in mind that the band at 620 mμ, observed in the colour test on concentrates, is shifted to 604—608 mμ in the presence of the unsaturated bodies existing in the unfractionated liver oils. There is also a band at 583 mμ which can be similarly displaced as far as 565 mμ. In most oils this band is near 572 mμ but it is almost completely masked by the 608 mμ maximum. Some oils are encountered in which the 572 mμ band predominates. The main conclusions arrived at in the above-mentioned investigations have been summarised by Morton and Heilbron [46] as follows : (1) The parallelism between the intensity of the 606 mμ band of the colour test and the intensity of the 328 mμ band of the spectrographic test breaks down so seriously in extreme cases as to render it improbable that the 606 mμ chromogen is vitamin A. (2) The 572 mμ chromogen and the substance responsible for the 328 mμ band are probably identical. (3) The blue colour obtained with rich oils and concentrates is often far deeper than it ought to be on the basis of correlation between the colour and the ultra-violet absorption. This is due to an increase in the 620 mμ chromogenic power, which may be due to a removal of inhibitors or to a real increase in the chromogen content on saponification. The relationship between this chromogen and vitamin A is obscure. (4) Many oils are encountered in which the blue colour is developed much more strongly if the oil has been allowed to stand for a few weeks, or has otherwise been subjected to oxidation processes. In such cases the 328 mμ band does not show a similar increase.

A statistical analysis [47] of all the data accumulated by biological, chemical, and spectrographic investigation of ten oils and three concentrates is regarded by Morton and Heilbron [48] as confirming beyond all reasonable doubt the claim of the 328 mμ band to be regarded as a direct property of vitamin A. Since the 583 mμ band of the colour test runs very closely parallel with the 328 mμ band it too must be accepted as a property of the vitamin. On the other

[45] R. A. Morton, I. M. Heilbron, and A. Thompson, *Biochem. J.*, 1931, **25**, 20; *A.*, 529; J. A. Lovern, R. H. Creed, and R. A. Morton, *ibid.*, p. 1341; *A.*, 1195; A. E. Gillam and R. A. Morton, *ibid.*, p. 1346; *A.*, 1195; I. M. Heilbron, A. E. Gillam, and R. A. Morton, *ibid.*, p. 1352; *A.*, 1195; J. A. Lovern and R. A. Morton, *ibid.*, p. 1336; *A.*, 1196.

[46] " Chemistry at the Centenary Meeting of the British Association," Heffer and Son, Cambridge, 1932.

[47] (Miss) K. H. Coward, F. J. Dyer, R. A. Morton, and J. H. Gaddum, *Biochem. J.*, 1931, **25**, 1102; *A.*, 1196.

[48] *Loc. cit.*

hand, there is little doubt that fish liver oils contain two chromogens active in the antimony trichloride test.

Enzymes.

J. B. S. Haldane [49] has published an interesting theoretical treatment of the molecular statistics of an enzyme action. K. Zeile and H. Hellström [50] have found that horse-liver catalase is an iron-porphyrin compound with a spectrum resembling that of alkaline hæmatin, and that its amount, reckoned in milligrams of combined iron, can be measured photometrically with great accuracy by converting it into pyridine-hæmochromogen. The assumption is made that each molecule of liver catalase contains only one atom of iron, and Haldane's mathematical treatment of the data of Zeile and Hellström leads him to the deduction that a molecule of catalase at 0° catalyses the destruction of about 2×10^5 hydrogen peroxide molecules per second. The mean life of the active catalase–hydrogen peroxide molecule is calculated to be about 10^{-7} second and the velocity constant for the union of catalase and hydrogen peroxide exceeds 7×10^6. These values are compared with similar data derived from other enzymes and from hæmoglobin. In concluding this remarkably interesting study, Haldane points out that, although enzymes in the cell are in general acting neither at their optimal temperature, p_H, nor substrate concentration, it would seem from the examples discussed that an enzyme molecule must commonly transform 100 or more substrate molecules per second. As a very active cell, such as baker's yeast, metabolises about 10^{-6} of a gram-molecule of oxygen per gram dry weight per second, we can get some idea of the possible complexity of the transformation undergone in it. If 5% of the dry weight of the cell consists of enzymes of an average molecular weight of 50,000, then 1 gram dry weight contains 10^{-6} gram-molecule of such enzymes, and less than 1% of this would be required for any particular process, for example, the activation of oxygen. In other words, the average atom, on its metabolic path through the cell, may be dealt with by more than 100 catalysts in succession.

Crystalline Urease.—An investigation of the chemical nature of crystalline urease has been published by E. Waldschmidt-Leitz and F. Steigerwaldt,[51] who have used the preparations first described by J. B. Sumner.[52] J. B. Sumner and K. Myrbäck [53] found it impossible

[49] *Proc. Roy. Soc.*, 1931, *B*, **108**, 559; *A.*, 1089.
[50] *Z. physiol. Chem.*, 1930, **192**, 171; *A.*, 123.
[51] *Ibid.*, 1931, **195**, 260; *A.*, 521.
[52] *J. Biol. Chem.*, 1926, **69**, 435; **70**, 97; *A.*, 1926, 1061, 1176.
[53] *Z. physiol. Chem.*, 1930, **189**, 218; *A.*, 1930, 1217.

to decide whether the purest crystalline urease obtainable consisted entirely of the enzyme, but found such urease to be as pure as the best invertase and to be readily prepared from crude material with a 700- to 800-fold increase in activity. Waldschmidt-Leitz and Steigerwaldt now find that, contrary to the statement of H. Tauber,[54] the crystalline material, which is of globulin character (confirming J. B. Sumner and D. B. Hand [55]), does not lose its activity when it is subjected to the action of trypsin and other proteolytic enzymes, although the globulin is hydrolysed. If, then, the crystalline globulin is not simply a carrier of the active urease, the supposition that the crystalline material is itself the enzyme is not warranted, since its breakdown products seem to retain the enzymic activity. Sumner has undoubtedly obtained highly active urease preparations in a crystalline form, but it is considered possible that the enzyme may be obtained free from admixed protein or protein-breakdown products.

Crystalline Pepsin and Trypsin.—J. H. Northrop [56] has described crystalline preparations of high peptic activity. These are protein in nature with an estimated molecular weight of 33,000 to 40,000. The nitrogen content, optical rotation, and proteolytic activity were constant for six different preparations and remained unchanged throughout seven recrystallisations. Data from solubility determinations in different salt solutions, the rate of inactivation by heat and alkali, and the determination of the diffusion coefficient suggest that the crystalline material is a pure substance, although the possibility that it is a solid solution cannot be excluded. The inactivation at p_H 10·5 and its reversal yield an active material possessing the same physical characteristics as the original material, which affords further evidence that the proteolytic activity is a property of the molecule itself. P. A. Levene and J. H. Helberger [57] find that after five recrystallisations the pepsin contains only 3·3% of its total nitrogen as basic nitrogen.

J. H. Northrop and M. Kunitz [58] have prepared from commercial samples of trypsin a crystalline protein which can digest casein and gelatin in neutral solution.

Enzymes and Dyes.—The affinity which certain dyes show towards enzymes has already been made the basis of a most useful method for purifying pepsin.[59] It seems that a study of the interactions of dyes

[54] *J. Biol. Chem.*, 1930, **87**, 625; *A.*, 1930, 1217.

[55] *J. Amer. Chem. Soc.*, 1929, **51**, 1255; *A.*, 1929, 723.

[56] *J. Gen. Physiol.*, 1930, **13**, 739, 767; 1931, **14**, 713; *A.*, 1930, 1317; 1931, 1090.

[57] *Science*, 1931, **73**, 494; *A.*, 984.

[58] *Ibid.*, p. 262; *A.*, 655.

[59] *Ann. Reports*, 1928, **25**, 244.

and enzymes may help in other ways to elucidate the structure and mode of action of the latter. The fact that certain dyes have specific toxic actions on enzymes, and on the catalytic activities of tissues, has been utilised by J. H. Quastel and A. H. M. Wheatley [60] in an investigation of the oxidation of a number of substrates by *B. coli*. E. Bamann and M. Schmeller [61] have observed that under certain conditions substances of the indicator type (phenolphthalein and bromothymol-blue) inhibit the hydrolysis of methyl butyrate by liver esterases. In Table VI are given some of the figures

TABLE VI.

Dye (1/5000).	Nature of dye.	Glucose.	Lactate.	Succinate.	Formate.
Malachite green ...	Basic	100	92	72	71
Brilliant green	,,	68	66	67	46
Methyl violet 6B ...	,,	100	88	46	86
Crystal violet	,,	97	91	53	92
Methylene blue	,,	57	33	75	28
Auramine	,,	93	87	51	54
Acriflavine	,,	100	95	45	58
Neutral red	,,	92	72	37	50
Chrysoidine	,,	95	34	19	44
Pyronine	,,	39	20	6	17
Safranine	,,	98	86	22	52
Bismarck brown ...	,,	0	4	8	27
Acid fuchsine	Acid	0	0	2	0
Acid green	,,	0	17	3	0
Soluble blue	,,	0	0	5	9
Water blue	,,	0	8	7	0
Orange G	,,	0	4	2	14
Crystal scarlet	,,	1	0	7	16
Congo red	,,	0	15	10	0
Benzopurpurine ...	,,	0	31	22	22

obtained by Quastel and Wheatley for the percentage inhibition by dyes of oxygen uptakes by *B. coli* in the presence of various substrates at p_H 7·4 and 37°.

The most important fact demonstrated by these results is that all the highly toxic dyes are basic, whilst the acid dyes have little or no action at the concentration and p_H employed. This leads to the conclusion that the dehydrogenases responsible for the activation of glucose, lactate, succinate and formate are essentially acidic in character. An exception is observed in the case of Bismarck brown, a tetrazo-dye which is basic, unlike the other two tetrazo-dyes (Congo red and benzopurpurine) included in the table. It is therefore apparent that, although basicity of the dye plays an important part in determining its combination with dehydrogenase, this is not the only factor involved; the structure of the dye molecule is also concerned. The action of dyes on the oxidation of succinate by

[60] *Biochem. J.*, 1931, **25**, 629; *A.*, 765.
[61] *Z. physiol. Chem.*, 1931, **194**, 1; *A.*, 392.

muscle tissue proved to be similar to that found with *B. coli*, but on the other hand dyes were without inhibitory action on the oxidation of succinate by brain tissue.

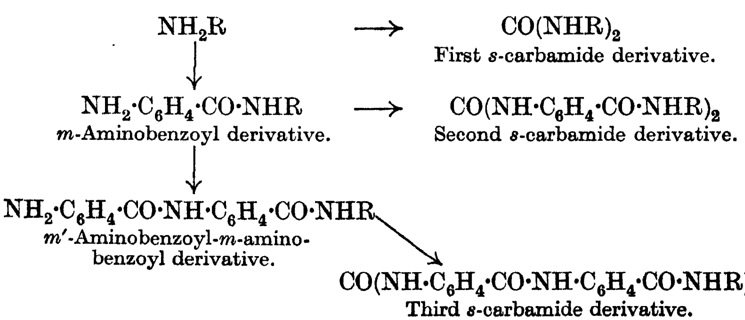
Selecting a particular enzyme of wide biological distribution, J. H. Quastel [62] has observed the action of dyes on fumarase, both in cell-free preparations and in the intact cell. Here a much greater specificity of behaviour of the dyes towards the enzyme is observed. Thus both basic and acidic dyes are toxic; among the acid dyes those of the Congo red series and of the triphenylmethane series are toxic, the former being the more effective. Congo red is toxic at a concentration of $1{\cdot}2 \times 10^{-8}$ *M*. Trypan-blue and trypan-red are likewise toxic. The enzyme present in the intact cell does not always show the same behaviour towards a given dye as when it is present in a cell-free extract. This difference is ascribed to the permeability of the cell membrane and is illustrated by the results quoted in Table VII. From this it would appear that *B. coli* is almost freely permeable to members of the triphenylmethane series, whereas it is resistant to Congo red and toluidine blue.

TABLE VII.

Comparison of Percentage Inhibitions effected by Dyes on Fumarase in the Cell Extract and in the Intact Cell (B. coli).

Dyes (1/5000).	Intact cell.	Cell extract.
Congo red	59	97
Methyl violet	88	82
Water blue	56	57
Toluidine blue	56	90

It is not to be supposed that Congo red and trypan-blue are general enzymic poisons; thus neither has a toxic action on urease. There must be some close relation between the structure of fumarase



and that of the Congo red series of dyes. This consideration led Quastel [63] to test the action on fumarase of other trypanocidal

[62] *Biochem. J.*, 1931, **25**, 898; *A.*, 983. [63] *Ibid.*, p. 1121; *A.*, 1188.

agents, not belonging to the Congo red series. The well-known trypanocide Bayer 205 was found to be toxic, but the main interest in this stage of the investigation lies in the actions of six naphthylaminedisulphonic acids and their *s*-carbamides synthesised by I. E. Balaban and H. King.[64] The free acids and their first *s*-carbamides (see formulæ) are inert. Toxicity begins to be apparent with the second carbamide derivatives (*s*-carbamide of *m*-aminobenzoylnaphthylaminedisulphonic acid) and is very marked with the third carbamide derivatives (*s*-carbamide of *m'*-aminobenzoyl-*m*-aminobenzoylnaphthylaminedisulphonic acid). Table VIII records some of the percentage inhibitions observed.

TABLE VIII.

Percentage Inhibitions of Fumarase Activity by Naphthylaminedisulphonic Acids and their s-*Carbamide Derivatives. Conc.* 1/4000.

	Freund's acid.	Amino-G-acid.	C-acid.	Amino-J-acid.	H-acid.	2R-acid.
Free acid	1	0	0	0	3	2
1st *s*-carbamide ...	—	—	3	4	—	5
2nd ,, ...	5	32	17	19	8	95
3rd ,, ...	83	90	94	95	22	95

Quastel draws attention to the parallelism which exists between the inhibition of the action of fumarase and trypanocidal action which, as was shown by Balaban and King, begins only at the second *s*-carbamide stage of combination and is most marked at the third stage. The parallelism with the substantive properties of these derivatives to cotton, which also increase from the first to the third carbamide stage, is most suggestive, and Quastel argues that there must be some structure in common between the fumarase enzyme, cotton fibre, and the trypanosome which makes for specific combination or adsorption.

Glyoxalase and Sodium Iodoacetate.—Attention was directed in the Report of last year [65] to Lundsgaard's investigations of the inhibitory action of iodoacetic acid on the formation of lactic acid by contracting muscle. Sodium iodoacetate is not a general enzymic poison. It does not affect glycogenolysis or the breakdown of phosphagen. It does not interfere with the action of ptyalin or invertase. It prevents the alcoholic fermentation by yeast without, however, affecting the oxidative metabolism. Lundsgaard formed the opinion, which has gained general acceptance, that iodoacetic acid is a specific inhibitor of glycolysis and therefore interferes with some stage of the degradation of glucose to lactic acid. These considerations led H. W. Dudley [66] to investigate the action of

[64] *J.*, 1927, 3068; *A.*, 1928, 164. [65] *Ann. Reports*, 1930, **27**, 259.
[66] *Biochem. J.*, 1931, **25**, 439; *A.*, 766.

sodium iodoacetate on the enzyme glyoxalase, detectable in practically all mammalian tissues, where it is active in the conversion of methylglyoxal into lactic acid. It is found to be a powerful inhibitor of this enzymic process, and the observation has an important bearing on the views advanced by H. D. Dakin and H. W. Dudley [67] regarding the possible rôle of methylglyoxal as the immediate precursor of lactic acid in the normal glycolytic chain of reactions. These views are obviously strengthened by Dudley's new observations, and it is suggested that sodium iodoacetate owes its power of interfering with normal glycolysis to its action as an inhibitor of glyoxalase.

Molecular Weights of Proteins.

From time to time in these Reports references have been made to the determination of the molecular weights of proteins.[68] These references were mainly to the work of T. Svedberg, whose ultracentrifugal method of measuring the rates of sedimentation of large molecules has been of the greatest service, and has in general yielded results in excellent agreement with those obtained by other methods where these have been available. In 1929 Svedberg [69] gave a short summary of his main results. He stated that all stable native proteins studied up till then might be grouped into two classes as follows : (1) Those with a molecular weight of the order of 10^6, such as hæmocyanin, and (2) those with a molecular weight of $35—210 \times 10^3$. The latter class is divisible into four sub-groups. The molecules of the first and fourth sub-group are spherical and have a radius of 2·2 and 4·0 mμ respectively, whilst those of the other sub-groups are not spherical. The spherical nature or otherwise of the molecule is deduced from a calculation of the molar frictional constant. The molecules of most of the members of the fourth sub-group are easily disaggregated by increasing the p_H. At the same time it was stated that a protein may, according to the p_H of the medium in which it is present, appear with the molecular mass, size, and shape of another protein.

A further communication by Svedberg [70] conveniently summarised his more recent work in this field. Most of the protein molecular-weight determinations had been carried out on material purified by the use of ammonium sulphate as a precipitating or crystallising agent. In the attempt to isolate lactalbumin from cow's milk it was observed that the molecular weight increased during purification, the figures obtained ranging from 12,000 to 25,000. It was found that the bulk of the native material in cow's milk, from which the

[67] *J. Biol. Chem.*, 1913, **15**, 463.

[68] *Ann. Reports*, 1925, **22**, 294; 1928, **25**, 235, 239; 1930, **27**, 34, 271.

[69] *Nature*, 1929, **123**, 871; *A.*, 1929, 835. [70] *Ibid.*, 1931, **128**, 999.

lactalbumin was formed, had a low molecular weight, probably not exceeding 1000, and that the progressive condensation to form larger molecular complexes was due especially to the action of the ammonium sulphate used in the purification. In view of this discovery the molecular weights of many of the proteins previously studied were re-examined without any chemical treatment, or at least under conditions closely resembling those of the native occurrence of the proteins. In the case of ovalbumin it was found that when egg-white is diluted with 1% sodium chloride solution, the sedimentation constant is always lower than that of purified ovalbumin, which is $3{\cdot}5 \times 10^{-13}$ and corresponds to a molecular weight of 34,500.[71] This value represents the upper limit of the condensation process in the case of this protein. On the other hand, blood serum diluted with 1% sodium chloride solution gives a sedimentation constant which is of the same order of magnitude as that of purified serum albumin and purified serum globulin. In the case of the vegetable seed protein amandin, a 10% sodium chloride extract of almonds showed the presence of a high-molecular protein with a sedimentation constant of the same order of magnitude as that of purified amandin, but a substance of much lower molecular weight was also found to be present. Hæmoglobin has in all cases given molecular weights of 68,000 and does not appear to be affected by the ammonium sulphate treatment. Phycocyan and phycoerythrin (*M*, 208,000) from algæ likewise have molecular weights which are unaffected by purification. The sedimentation constant of hæmocyanin is 98×10^{-13} and is constant under various conditions, as, for instance, in the undiluted blood of *Helix pomatia* (protein concentration 3%), in the blood diluted with 1% sodium chloride solution (protein concentration 0·1%), and in purified hæmocyanin. This protein is therefore present in the blood of *Helix* with the same enormous molecular weight, namely, 4,930,000, as in purified hæmocyanin.

The general conclusion made from these observations is that most proteins do possess the same molecular weights in their native state as in the purified laboratory products. On the other hand, there are instances of the protein existing in the living organism as a low-molecular pro-protein which may be converted into the real protein by the " purification " process, especially by the action of ammonium sulphate.

Attention is called by W. T. Astbury and H. J. Woods [72] to an interesting theoretical aspect of these results on protein molecular

[71] See also J. B. Nichols, *J. Amer. Chem. Soc.*, 1930, **52**, 5176; *A.*, 374; B. Sjögren and T. Svedberg, *ibid.*, p. 5187; *A.*, 374.

[72] *Nature*, 1931, **127**, 663; *A.*, 752.

weights. The sequence of the numbers 1, 2, 3, and 6 as multiples of Svedberg's value of 34,500 is discussed in relation to the peptide chain and its possible crystallographic combinations. It is considered that the value 34,500 is due to the vibrational instability of peptide chains of length greater than a certain limit. The disruptive action of high energy quanta on the length and cohesion of these peptide chains is shown in experiments on unstretched wool, which, after exposure for many hours to the full beam of a Shearer *X*-ray tube, shows many of the properties of wool which has been exposed under tension to the action of steam.

From an examination by means of the ultra-centrifuge of the protein fractions obtained by electrodialysis of serum, P. von Mutzenbecher [73] has obtained results which are in accord with the views of Svedberg. Both the water-soluble and the water-insoluble fraction are found to be polydisperse and the specific rate of sedimentation of the water-soluble fraction varies greatly, but lies between those found for serum globulin and albumin prepared by salting out with ammonium sulphate. The insoluble fraction contains several components of high molecular weight and the results obtained for this fraction agree well with those found by T. Svedberg and B. Sjögren [74] for euglobulin prepared in another way. From the soluble fraction, after the removal of the pseudoglobulin, slightly impure crystalline albumin can be obtained. Both the soluble fraction and the pseudoglobulin have higher rates of sedimentation in electrolyte-free solutions than in solutions containing electrolytes, and both contain appreciable amounts of components of high molecular weight. Fractionation of the serum proteins by removal of electrolytes therefore does not lead to the production of monodisperse systems. Only in a solution containing salts is a homogeneous globulin molecule stable. The general conclusion is that for the fractionation of the proteins of serum electrodialysis is not a sufficiently protective method.

On the other hand, results which do not accord well with the foregoing have been recorded by G. S. Adair and M. E. Robinson [75] in an analysis of the osmotic pressures of serum proteins. It is stated that serum albumin can be recrystallised four times without change in the molecular weight. The mean value of the molecular weight of horse serum albumin is 72,000 $\pm$ 3,000. Similar values are found for the albumins of ox and sheep sera. The mean value of the molecular weight of the unfractionated globulin of the horse is 175,000, and the unfractionated globulins of the ox and the sheep

[73] *Biochem. Z.*, 1931, **235**, 425; *A.*, 1175.
[74] *J. Amer. Chem. Soc.*, 1930, **52**, 2855; *A.*, 1930, 1197.
[75] *Biochem. J.*, 1930, **24**, 1864; *A.*, 248.

give similar results. Euglobulin prepared by a rapid method is found to resemble total globulin, so that Svedberg's value for total globulin, namely, 103,800, is lower than that found by Adair and Robinson, who conclude that the state of aggregation of the proteins in the untreated serum appears to be the same as their state of aggregation in the purified proteins prepared by the methods used in these investigations. It must none the less be conceded that Svedberg's views furnish us, in certain cases, with a conception of the protein as a labile molecule, which seems a fitting physical basis for its biological rôle.

A study of horse serum globulin from a rather different standpoint has been published by J. W. McBain and E. Jameson,[76] who have analysed their observations in a phase diagram. It is found that there is a great similarity to the behaviour of soap, both in respect of the forms of globulin and soap which separate and in the shapes of the areas representing the solutions of the two substances. Globulin solution, euglobulin, and pseudoglobulin are regarded as being three phases of the same substance, dehydrated globulin. A solution of globulin is the ordinary isotropic solution, whilst euglobulin and pseudoglobulin are liquid crystalline phases, or a liquid and a glass which are slightly doubly refracting.

The Molecular Weight of Insulin.—T. Svedberg and B. Sjögren [77] have investigated by ultracentrifugal methods the molecular weight of insulin, using a crystalline preparation for the purpose. Over a p_H range of 4·5 to about 7·0, insulin is stable and its sedimentation constant has a value of $3{\cdot}47 \times 10^{-13}$. Outside its stability range dissociation into low molecular products takes place, but this dissociation is reversible if the substance has not been brought too far into the acid or alkaline region and has not been kept there too long. At p_H 6·7—6·8 a mean value for the molecular weight of 35,100 is found. The molecule is spherical. It is concluded that crystalline insulin is a homogeneous and well-defined protein of the ovalbumin class, and that its synthesis is therefore a very remote possibility. It may be remarked in passing that the experiments of A. F. Charles and D. A. Scott [78] and of W. Corneli,[79] on the action of proteolytic enzymes on insulin, have not so far yielded any evidence of the hydrolysis of insulin into smaller and physiologically active molecules.

[76] *Trans. Faraday Soc.*, 1930, **26**, 768; *A.*, 376.

[77] T. Svedberg, *Nature*, 1931, **127**, 438; *A.*, 658; B. Sjögren and T. Svedberg, *J. Amer. Chem. Soc.*, 1931, **53**, 2657; *A.*, 1096.

[78] *Trans. Roy. Soc. Canada*, 1930, [iii], **24**, v, 95; *A.*, 397.

[79] *Z. physiol. Chem.*, 1931, **199** 217; *A.*, 1194.

A New Synthesis of Methionine.

The amino-acid methionine, first isolated by Mueller in 1922, was synthesised by Barger and Coyne.[80] A second synthesis has been described by W. Windus and C. S. Marvel.[81] Neither of these methods, however, made the substance more easily available than the natural product, which is very troublesome to isolate. G. Barger and T. E. Weichselbaum [82] have now described an improved method of synthesis which gives a yield of 58% on the basis of the β-chloro-α-methylthiolethane employed. The latter is made to react with ethyl sodiophthalimidomalonate and the resulting compound (I) is hydrolysed first with alkali to yield the phthalamidomalonic acid (II) and then with acid to yield methionine (III) :

$$CH_3{\cdot}S{\cdot}CH_2{\cdot}CH_2Cl + Na{\cdot}C(CO_2Et)_2{\cdot}N{<}{}^{CO}_{CO}{>}C_6H_4$$

$$\downarrow$$

$$CH_3{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}C(CO_2Et)_2{\cdot}N{<}{}^{CO}_{CO}{>}C_6H_4 \qquad \text{(I.)}$$

$$\downarrow \text{NaOH}$$

$$CH_3{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}C(CO_2H)_2{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H \qquad \text{(II.)}$$

$$\downarrow \text{HCl}$$

$$CH_3{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H \qquad \text{(III.)}$$

d-3 : 5-*Di-iodotyrosine as a Constituent of the Thyroid Protein.*

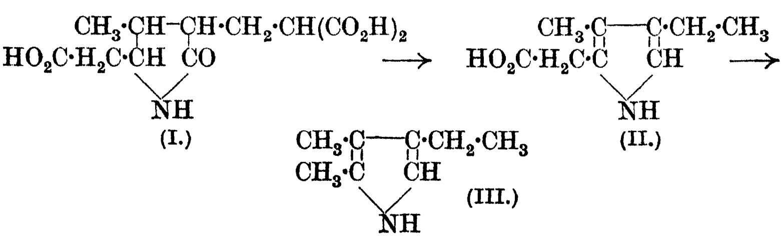
The previous work of Harington has been summarised in earlier Reports.[83] During the past year C. R. Harington and S. S. Randall [84] have recorded the isolation of *d*-3 : 5-di-iodotyrosine from the protein of the thyroid gland. They were able to secure the optically active acid by making use of proteolytic enzymes. Harington and Randall [85] have already described the isolation of *dl*-di-iodotyrosine by means of the graduated hydrolysis of the thyroid gland material with barium hydroxide. This work was repeated shortly afterwards by G. L. Foster,[86] who obtained 33% of the total iodine of the gland as di-iodotyrosine and 16% as thyroxine. The materials now used by Harington and Randall for the isolation of the optically active acid were the various mother-liquors containing acid-soluble organically combined iodine which were obtained as by-products in the

[80] *Ann. Reports*, 1928, **25**, 233; *Biochem. J.*, 1928, **22**, 1417; *A.*, 1929, 175.
[81] *J. Amer. Chem. Soc.*, 1930, **52**, 2575; *A.*, 1930, 1026.
[82] *Biochem. J.*, 1931, **25**, 997.
[83] *Ann. Reports*, 1926, **23**, 234; 1928, **25**, 261; 1930, **27**, 274.
[84] *Biochem. J.*, 1931, **25**, 1032; *A.*, 1178.
[85] *Ibid.*, 1929, **23**, 373; *A.*, 1929, 839.
[86] *J. Biol. Chem.*, 1929, **83**, 345; *A.*, 1929, 1191.

course of the isolation by Harington and Salter [87] of *l*-thyroxine by the enzymic digestion of that thyroid gland. The filtrates from the peptic digestion of crude iodothyreoglobulin, after fractionation with silver nitrate, yielded a product which was subjected to tryptic digestion and finally to the action of erepsin. After this treatment it was possible, by a simple fractionation, to separate *d*-di-iodotyrosine in a pure condition. It showed in *N*-hydrochloric acid $[\alpha]_{5461} + 3{\cdot}85°$. We therefore now have evidence that both *l*-thyroxine and *d*-3 : 5-di-iodotyrosine are constituent amino-acids of the characteristic protein of the thyroid gland. These are the only two iodine-containing compounds of the thyroid gland and the iodine would normally appear to be about equally distributed between them, although variations in such distribution may occur and would account for discrepancies between iodine content and physiological activity of thyroid preparations.

A New Tribasic Acid present in Liver Extracts.

Last year there was described the isolation from liver extracts by H. D. Dakin and his co-workers [88] of a dipeptide of β-hydroxyglutamic acid and γ-hydroxyproline. This substance, which was obtained as a crystalline quinine salt, produced a strong reticulocyte response in cases of pernicious anæmia. In the course of the earlier work evidence was obtained of the presence of a second quinine salt of higher quinine content. This has now been isolated by H. D. Dakin and R. West [89] in a crystalline condition and is differentiated from the first-described quinine salt by its higher melting point and optical rotation, its lower solubility in water, and the fact that it gives no amino-nitrogen on hydrolysis. The free acid is provisionally considered to have the formula (I). When the acid is administered intravenously to cases of pernicious anæmia in the form of a single dose (0·25 to 0·75 g.), it is found that a distinct rise in reticulocytes



sometimes follows. But the response is neither as prompt nor as quantitatively striking as that following the administration of

[87] *Ann. Reports*, 1930, **27**, 274. [88] *Ibid.*, p. 273.
[89] *J. Biol. Chem.*, 1931, **92**, 117; *A.*, 974.

structurally related substances, a description of which is promised later. The new acid is not regarded as being responsible for any large share in the reticulocyte response evoked by liver extracts.

On the other hand, Dakin and West attach some importance to the acid as a possible precursor of the porphyrin nucleus of hæmoglobin. When the acid was heated in a sealed tube with excess of baryta at 120—130° there was obtained an ether-soluble pyrrolecarboxylic acid, $C_9H_{13}O_2N$, which was isolated as the picrate (provisional formula II). At 155—165°, hæmopyrrole was produced (provisional formula III). Dakin and West point out that the methylmalonic acid side chain present in the new acid occurs in each of the four pyrrole rings of uroporphyrin. From the chemical standpoint the acid would therefore appear to be more directly allied to uroporphyrin than to coproporphyrin or hæmatoporphyrin, since the synthesis of the latter substances would require the elimination of 4 and 6 molecules of carbon dioxide respectively from each group of four pyrrole rings in the porphyrin nucleus.

The Female Sexual (*Œstrous-producing*) *Hormone.*

When the Report of last year was written the position with regard to the œstrous-producing hormone was that A. Butenandt and G. F. Marrian had both satisfactorily characterised their active crystalline preparations as $C_{18}H_{22}O_2$ and $C_{18}H_{24}O_3$ respectively.[90] It was clear that the two workers were handling different but very closely related substances. Marrian had identified the substance $C_{18}H_{24}O_3$ as a trihydric alcohol with one phenolic hydroxyl, whilst Butenandt's substance, with one molecule of water less than Marrian's, was shown to be a hydroxy-ketone. A. Butenandt and F. Hildebrandt [91] have now succeeded in isolating Marrian's substance by his method from a chloroform extract of the urine of pregnancy, and from the residual oil obtained from the isolation of Butenandt's own substance. The latter substance ($C_{18}H_{22}O_2$) has also been obtained by B. Skarżyński,[92] whilst S. A. Thayer, L. Levin, and E. A. Doisy [93] have also described, in a paper which makes rather inadequate reference to the work of Marrian and of Butenandt,[94] the isolation of the $C_{18}H_{24}O_3$ substance. Butenandt and Hildebrandt have converted, by distillation with potassium hydrogen sulphate, the $C_{18}H_{24}O_3$

[90] *Ann. Reports*, 1930, **27**, 271.

[91] *Z. physiol. Chem.*, 1931, **199**, 243; *A.*, 1195.

[92] *Ibid.*, 1931, **196**, 19; *A.*, 771.

[93] *J. Biol. Chem.*, 1931, **91**, 655; *A.*, 879 (see also E. A. Doisy and S. A. Thayer, *ibid.*, p. 641; *A.*, 879).

[94] A. Butenandt and G. F. Marrian, *Z. physiol. Chem.*, 1931, **200**, 277; *A.*, 1337; G. F. Marrian and A. Butenandt, *Nature*, 1931, **128**, 305; *A.*, 1337.

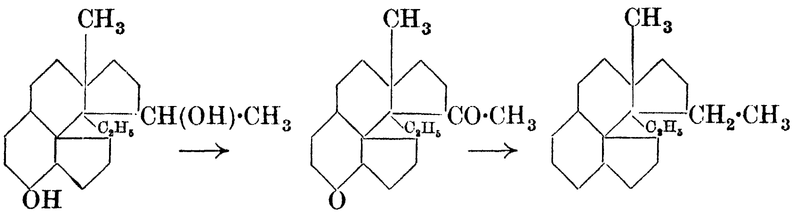
substance into the $C_{18}H_{22}O_2$ substance identical with that isolated directly from the urine. The dehydrated substance is now characterised as the follicular hormone (dioxyœstrin) and the other as its hydrate (trihydroxyœstrin). It appears that the physiological activity of the hydrate is much lower than that of the hormone and decreases with purification. Thus the hydrated product with a melting point of 276° and $[\alpha]_D + 34{\cdot}4°$ has only 2% of the activity of the hormone, but, on the other hand, the hormone prepared by distillation of this hydrate is fully active. The two forms—the hormone and its hydrate—are not interconvertible by any of the steps used in their isolation and both must therefore be present in the urine of pregnancy.

The hormone $C_{18}H_{22}O_2$, like the hydrate, is acidic and G. F. Marrian and G. A. D. Haslewood [95] have shown that this acidity is due to the phenolic hydroxyl group. Thus by subjecting trihydroxyœstrin (1) to the dehydrating action of distillation with potassium hydrogen sulphate, followed by methylation with methyl sulphate, and (2) to methylation, followed by dehydration, they have obtained by these alternative procedures products yielding identical oximes. The dehydration product of trihydroxyœstrin monomethyl ether is therefore identical with dioxyœstrin monomethyl ether. This proves that in the conversion of trihydroxyœstrin into dioxyœstrin water is eliminated from the two non-acidic hydroxyl groups of the former. It also shows that the acidity of dioxyœstrin is due to the phenolic hydroxyl group and not to enolisation of the carbonyl group.

In addition to the œstrous-producing substance decribed above, both Marrian and Butenandt isolated from the urine of pregnancy a second, but physiologically inactive, crystalline substance which proved to be a saturated dihydric alcohol.* Butenandt called this substance pregnandiol and assigned to it the composition $C_{21}H_{36}O_2$. On oxidation there was formed the saturated diketone, $C_{21}H_{32}O_2$, pregnandione, and by Clemmensen reduction of the latter A. Butenandt, F. Hildebrandt, and H. Brücher [96] have obtained the corresponding hydrocarbon, $C_{21}H_{36}$, pregnane. These workers have also prepared the same hydrocarbon by reduction, with zinc amalgam and hydrochloric acid, of ætiocholyl methyl ketone, $C_{21}H_{34}O$, obtained from cholanic acid. On the basis of these results a close affinity of pregnandiol with the basic ring systems of the bile acids

[95] *J. Soc. Chem. Ind.*, 1931, **50**, 1044.
[96] *Ber.*, 1931, **64**, [*B*], 2529.
* The Reporter was in error in confusing, in the Report of last year, this inactive substance with the active crystalline material (see *Ann. Reports*, 1930, **27**, 272, lines 1, 2, 22, 23).

is deduced, and the formulæ appended are ascribed to the alcohol, the diketone, and the hydrocarbon :



Pregnandiol Pregnandione Pregnane

Pregnandiol is thus a neutral oxidation product of the bile acids or sterols. It is sterically related to the coprosterol–cholanic acid series. It is not found in male urine nor in normal female urine. On the other hand it is absent from the urine of the pregnant mare, and the indications are at present against a specific association of this interesting alcohol with the condition of pregnancy.

Specific Carbohydrates and Immunology.

(Continued from *Ann. Reports*, 1929, **26**, 239—241.)

W. F. Goebel and O. T. Avery [97] have described the synthesis of the *p*-aminobenzyl ether of the specific polysaccharide of Type III pneumococcus and the coupling of the ether, by means of the diazo-reaction, with protein. The steps in the process involved the interaction of *p*-nitrobenzyl bromide and the polysaccharide, the reduction of the ether so obtained to give the *p*-aminobenzyl ether, the diazotisation of the latter, and finally the alkaline coupling of the diazonium chloride with the protein. The protein used was serum globulin and the immunological specificity of the "synthetic antigen" so obtained has been studied by O. T. Avery and W. F. Goebel.[98] The remarkably interesting result emerges that the synthetic antigen shows, in rabbits, the type-specific antipneumococcus response which neither one of its constituents alone is capable of inciting when injected singly into these animals. It must be borne in mind that the carbohydrate alone, although specific in its reactions, has not been shown to be antigenic, that the antigen used in these investigations has in common with the Type III pneumococcus only the specific capsular polysaccharide, and that the protein to which it is conjugated is of widely remote biological origin. Rabbits immunised with the synthetic antigen acquire an active immunity against infection with virulent Type III pneumococci, and the sera of such immune rabbits contain type-specific anti-substances which (a)

[97] *J. Exp. Med.*, 1931, **54**, 431. [98] *Ibid.*, p. 437.

precipitate the Type III capsular polysaccharide, (b) agglutinate Type III pneumococci, and (c) specifically protect mice against Type III infection. These results afford strong evidence in favour of the view that an effective, active immunity can be developed in which the only antibacterial anti-substances formed are those directed against the capsular polysaccharide.

Avery and Goebel are careful to point out that in the present state of our knowledge it would be hazardous to predict the precise conditions under which complex carbohydrates by themselves may function as antigens, and that their present study simply defines certain conditions under which the Type III pneumococcus polysaccharide, in chemical union with a foreign protein, is rendered specifically antigenic in animals in which the carbohydrate alone has never been found to incite anti-substance formation. That such caution is wise is shown by a claim of J. Zozaya,[99] who states that the anthrax specific polysaccharide adsorbed on collodion particles is antigenic.

Further advances in the chemical characterisation of the specific and non-specific polysaccharides of Type IV pneumococcus have been recorded by M. Heidelberger and F. E. Kendall.[99a]

Plant Biochemistry.

Mineral Nutrients and their Effects on Plant Growth.

Mechanism of the Intake of Minerals.—Much attention continues to be devoted to the complex problem of the manner in which the root cell membranes of plants exert an apparent selective power in their permeability to electrolytes and are enabled to maintain within the tissues a higher salt concentration than exists in the surrounding medium.

W. J. V. Osterhout [1] maintains his view that the actual penetration of electrolytes takes place in the molecular condition. Thus the accumulation of potassium chloride in *Valonia* results from the entry of molecular potassium hydroxide, its combination with weak acids within the cell and subsequent conversion into potassium chloride by hydrochloric acid molecules which have penetrated separately. The relative permeabilities of basic molecules are assumed to depend on their respective thermodynamic potentials.

The weight of general opinion, however, favours the view that the penetration of electrolytes is an ionic phenomenon, an interesting theoretical discussion of which is given by G. E. Briggs.[2] The

[99] *Science*, 1931, **74**, 270; *A.*, 1335.

[99a] *J. Exp. Med.*, 1931, **53**, 625; *A.*, 1335.

[1] *J. Gen. Physiol.*, 1930, **14**, 285, 301; *A.*, 129.

[2] *Proc. Roy. Soc.*, 1930, *B*, **107**, 248; *A.*, 129.

suggestion is made that cell membranes exhibit alternating phases of permeability favouring the entry of anions and kations respectively.

The more practical aspects of this problem in its relation to the nutrient condition of soils further involve consideration of quantitative water movements associated with the entry of electrolytes. In this connexion the work of J. F. Breazeale[3] on the absorption of nutrients by plants at low soil-moisture conditions is of value. A continuous film of moisture is assumed to exist between the soil and the root hairs at all moisture contents above the wilting point. The passage of ions from soil solution to plant is controlled by their electrical charges and does not necessarily involve the simultaneous entry of water. Provided sufficient water remains in the soil to maintain the system, the water consumption of the plant is to a large extent an independent process. Interesting support for this view is given by the observation that plants may take in water through portions of the root system located in moist soil and exude water from other rootlets situated in a drier soil area. On the other hand, there is indirect evidence of a close relationship between the intake of water and of electrolytes by plants, typical of which is the observation of B. S. Meyer[4] that the addition of soluble salts to soil produces a marked decrease in the water requirement of cotton plants, which is roughly proportional to the amount of salt added.

It is now generally conceded that plants can absorb electrolytes with as much or possibly even greater ease from dilute solution as from more concentrated ones and that with the possible exception of phosphates[5] the mineral nutrients are present in natural soil solutions in sufficient quantity for the normal growth of plants. W. U. Behrens[6] points out that the intake of nutrients from solutions of this order of dilution involves the expenditure of free energy which is presumably available from chemical reactions taking place within the cell.

A critical survey of current views on the mineral intake of plants and of their relationship to laboratory methods for the examination of the nutrient status of soils is given by D. R. Hoagland.[7]

Nitrogen Assimilation.—The vexed question of the relative values of ammonia and of nitrates in plant nutrition has received considerable attention recently. Although the direct intake of ammonium

[3] *Arizona Agric. Exp. Sta. Tech. Bull.*, 1930, No. 29, 137; *A.*, 535.
[4] *Amer. J. Bot.*, 1931, **18**, 79; *A.*, 882.
[5] F. W. Parker and W. H. Pierre, *Soil Sci.*, 1928, **25**, 337; *B.*, 1928, 534.
[6] *Z. Pflanz. Düng.*, 1928, **11**, *A*, 93, 150; *B.*, 1928, 683.
[7] *Plant Physiol.*, 1931, **6**, 373; *A.*, 1201.

salts is now generally recognised, as also is Prianishnikov's conception that ammonia represents the first essential stage in plant metabolism, it is doubtful whether agricultural chemists in general are yet prepared to accept his view that the principal function of nitrates in plant nutrition is to provide an alternative and less toxic source of nitrogen to act as a regulator of the ammonia concentration within the cells.[8] Among numerous investigations of the relative rates of intake of ammonium and nitrate ions by plants, some divergence of opinion is apparent. This is traceable in some cases to that ever-recurring source of confusion, *viz.*, the comparison of results of water cultures and soil cultures, and in others to the fact that assimilation rates as judged by the removal of ions from culture solutions and as measured by the growth rates of plants are based on two very distinct functions.

Both the nitrate and the ammonium ions appear to be more readily absorbed from dilute solutions, *e.g.*, 0·0005*N*, than from more concentrated ones,[9] and under similar conditions ammonia absorption predominates in the younger stages of plant growth and that of nitrate later.[10, 11, 12]

Nitrogen assimilation is largely dependent on the reaction of the nutrient. From neutral or slightly acid solutions, any difference in the ease of assimilation of nitrate or ammonium ions is in favour of the latter. The intake of nitrates is much less affected by extremes of reaction and predominates in media of $p_H < 5·0$ and $> 7·0$. The optimum reaction for the intake of both forms of nitrogen is p_H 6·0 approx.[13, 14, 15, 16] The reduced efficiency of ammonium salts in very acid media ($p_H < 3·6$) recorded by W. Mevius [17] is attributed to an unusually rapid intake of ammonia under these conditions and to the production of a toxic alkalinity in the root sap. A similar explanation is offered by Willis and Davies [18] for the depressed plant yields resulting from feeding with very concentrated solutions of urea.

In an interesting paper by M. K. Domontovitsch and A. I. Groschenkov,[19] it is shown that nitrogen supplied as ammonium sulphate

[8] *Trans. Sci. Inst. Fert. (Moscow)*, 1929, No. 61, 99; *B.*, 1930, 74.
[9] K. Schmid, Diss., Hohenheim, 1930; *B.*, 989.
[10] J. A. Naftel, *J. Amer. Soc. Agron.*, 1931, **23**, 142; *B.*, 603.
[11] T. L. Loo, *J. Fac. Agric. Hokkaido*, 1931, **30**, I, 1; *B.*, 1149.
[12] L. G. Willis and E. A. Davies, *N. Carolina Agric. Exp. Sta. Tech. Bull.* 1928, No. 30.
[13] J. A. Naftel, *loc. cit.* [14] T. L. Loo, *loc. cit.*
[15] D. Prianishnikov, *Biochem. Z.*, 1929, **247**, 341; *A.*, 1929, 728.
[16] K. Pirschle, *Ber. deut. bot. Ges.*, 1929, **47**, 86; *A.*, 1930, 262; *Z. Pflanz. Düng.*, 1931, **22**, *A*, 51; *B.*, 1022.
[17] *Z. Pflanz. Düng.*, 1928, **10**, *A*, 208; *B.*, 1928, 278.
[18] *Loc. cit.* [19] *Z. Pflanz. Düng.*, 1929, **14**, *A*, 194; *B.*, 1929, 788.

produced greater dry matter yields than as sodium nitrate but the ratio of root : total plant was greater in the case of nitrate. Moreover the effect of light in increasing dry matter production was greater when nitrogen was supplied as nitrate than as ammonium salts. That factors other than reaction and concentration of the medium affect the crop-producing efficiency of nitrates and of ammonia is indicated by I. G. Dikussar.[20] He records that in a series of media containing increasing proportions of potassium, calcium, and magnesium salts the efficiency of ammonium sulphate rises steadily in media of p_H 5·5 but declines in those of p_H 7·0. Under similar conditions, increasing salt concentrations have no effect on the efficiency of sodium nitrate at p_H 5·5 but improve it at p_H 7·0. It is also shown that the ash constituents of plants receiving nitrogen as ammonium sulphate are less than when sodium nitrate is supplied. The ammonium ion is said to reduce the permeability of roots to calcium and magnesium. In a comparison of the efficiencies of several forms of nitrogen the same author records that, under the conditions of his experiments, ammonium sulphate produced the heaviest yields at p_H 7·0, whereas at p_H 5·5 the order of efficiency was sodium nitrate $>$ ammonium nitrate $>$ sodium nitrite $>$ ammonium sulphate. In a more recent paper Prianishnikov (*Udobr. Urozhai*, 1931, **3**, 53) records best growth of beet at p_H 7·0, using ammonium sulphate, and at p_H 5·5, using sodium nitrate. In acid media the use of ammonium salts reduced the intake of calcium, the effect being counteracted by additions of calcium sulphate. With sodium nitrate as the source of nitrogen, increasing concentrations of calcium, magnesium, and potassium salts in the nutrient reduced the yields. In a somewhat similar investigation Pirschle,[21] in his more recent paper, shows that ammonia assimilation is associated with a relatively greater phosphate intake, and that of sodium nitrate with a greater potash intake. It is significant that better growth was produced by mixtures of ammonium salts, nitrate and urea than by either ammonium salts or nitrate alone.

The utilisation of nitrites by plants is examined by W. Mevius and I. Dikussar,[22] who show that in neutral or alkaline solution maize can utilise nitrites without metabolic disturbances, since the distribution of nitrogen in the plant tissues appears normal in relation to the nitrogen intake. The optimum nitrite concentration is approx. 50 p.p.m. at p_H 7·0. With high concentrations of nitrite protein synthesis is retarded and there follows an accumulation, within the tissues, of amides and ammonia but *not* of nitrite.

[20] *Landw. Jahrb.*, 1930, **72**, 79; *B.*, 1930, 961.
[21] *Loc. cit.*
[22] *Jahrb. wiss. Bot.*, 1930, **73**, 633; *B.*, 989.

Amino-acids may also be assimilated by plants.[23] They are not, however, equally utilisable, glycine and alanine being inferior to asparagine and aspartic and glutamic acids.

Intake and Effects of Potassium.—A relatively small number of papers fall to be considered in this section. In connexion with the practical use of fertilisers the question of the "physiological" reaction of potassium salts arises, and reference should be made to the work of M. Górski and O. Dabrowska.[24] The physiological effect of potassium chloride is shown to be influenced by the reaction of the nutrient medium both directly and also indirectly through its action on the anion intake of plants. In media of p_H 5·7—7·1 potassium chloride solutions are physiologically acid to plants and at p_H <4·4 definitely alkaline.

The minimum concentration of potassium in nutrients requisite to produce optimum growth is of considerable interest in connexion with soil solution investigations. R. P. Bartholomew and G. Janssen [25] have examined this for a number of crops and obtained values varying from 0·5—3·0 p.p.m. The fact that symptoms of potash starvation are less frequent than might be anticipated during the rapid intake of potassium from such dilute solutions is explained by the rapidity of internal transport of potash from older to the more rapidly growing tissues.

No confirmatory evidence of the selective adsorption of the isotope K^{41} by plants [27] was obtained as the result of examinations of sugar beet by K. Heller and C. L. Wagner [28] or of cotton and wheat by H. H. Lowry.[29]

Intake of Phosphate.—The doubt expressed by N. Comber, F. W. Parker, and others whether the phosphate concentration in the soil solution was such as to provide for adequate plant growth has been one of the principal stumbling blocks to the belief that the mineral intake of plants is entirely in the dissolved condition. Further light is thrown on this problem by the work of J. W. Tidmore,[30] who finds that satisfactory crops of maize, tomato, and sorghum may be produced in soils having <0·05 p.p.m. of phosphate in the displaced soil solution, whereas in culture solutions a concentration of 0·1 p.p.m. is necessary: L. J. H. Teakle [31] doubts the possibility of a direct relation between the phosphate intake

[23] *Ergeb. Agrik.-chem.*, 1930, **2**, 143; *B.*, 821.
[24] *Poln. Jahrb. Land- u. Forstwirts.*, 1930, **24**, 46; *B.*, 456.
[25] *Proc. Assoc. Southern Agric. Workers*, 31st Conv., 1930, 242; *B.*, 647.
[27] F. H. Loring and J. G. F. Druce, *Chem. News*, 1930, **140**, 34.
[28] *Z. anorg. Chem.*, 1931, **200**, 105; *A.*, 1342.
[29] *J. Amer. Chem. Soc.*, 1930, **52**, 4332; *A.*, 141.
[30] *J. Amer. Soc. Agron.*, 1930, **22**, 481; *A.*, 83.
[31] *Plant Physiol.*, 1929, **4**, 213.

of plants and the concentration of phosphate in the nutrient medium. If such a relationship exists, it seems likely to lie within the range 0·1 to 1·0 p.p.m. of phosphate in the medium. A similar figure is arrived at by F. W. Parker and W. H. Pierre.[32]

Relationships between the intake of phosphates and of other mineral nutrients were examined by O. Owen [33] during investigations of the possible use of the tomato as an indicator of the nutrient requirement of soils. A relationship exists between the supply of potash in soils and the intake of phosphate and vice versa. The phosphate and potassium contents of the leaves of the tomato are inversely related, whereas in the fruit the relationship is probably direct. S. H. Eckerson,[34] also working with tomatoes, gives a further instance of the inter-related effects of nutrients and of the difficulty attending the interpretation of results of direct observations of plant growth. Plants supplied with adequate nitrate but deficient phosphate show symptoms of nitrogen starvation. In this case phosphate exhaustion is followed by a cessation of catalase activity and the breakdown of normal metabolism is shown by the accumulation of nitrates, sugars, and starches and an increasing acidity.

Secondary Plant Nutrients.—Boron. The essential character of boron in the mineral nutrition of plants has been emphasised in recent years by Haas and his colleagues with citrus, by E. S. Johnson [35] with potatoes and tomatoes, and by T. R. Swanbach [36] with tobacco.

The minimum requirement of boron in nutrient solutions set by A. L. Sommer and C. B. Lipman [37] at 0·5 p.p.m. has since been confirmed by several workers. The effects of boron deficiency seem varied. A. L. Sommer and H. Sorokin [38] record abnormal root development and extensive changes in the structural tissues. A. R. C. Haas and L. J. Klotz [39] show that boron is essential to cell division in the meristematic tissue of growing points, and in an interesting paper from A. I. Smirnow,[40] boron is shown to regulate the growth of stems with respect to root and leaves in tobacco. No effect on nitrogen storage or metabolism in tobacco could be ascribed to

32 *Loc. cit.*

33 *J. Agric. Sci.*, 1931, **21**, 442; *A.*, 1200; *ibid.*, 1929, **19**, 413; *B.*, 1929, 732.

34 *Contr. Boyce Thompson Inst.*, 1931, **3**, 197; *A.*, 1200.

35 *Soil Sci.*, 1928, **26**, 173; *B.*, 1929, 222; also (with Doré), *Science*, 1928, **67**, 324.

36 *Plant Physiol.*, 1927, **2**, 475.

37 *Ibid.*, 1926, **1**, 231.

38 *Ibid.*, 1928, **3**, 237; *A.*, 1929, 855.

39 *Hilgardia*, 1931, **5**, No. 8, 175; *A.*, 1340.

40 *U.S.S.R. State Inst. Tobacco Invest. Bull.*, 1930, No. 30; *B.*, 457.

boron. Relationships between boron deficiency and susceptibility to disease in plants are indicated by F. M. Eaton.[41] Spot blotch in cereals did not appear in cultures free from boron, but increased in intensity with the amount of that element applied. On the other hand, powdery mildew appeared only in the absence of boron. Chemical features of boron deficiency include increasing gum formation and high carbohydrate accumulation in leaves. In any general consideration of experimental results of this nature due regard must be paid to the significant observation of A. R .C. Haas[42] that plants can usually obtain sufficient boron for normal growth from the glaze of the earthenware jars frequently used in plant culture investigations.

Copper. Beneficial effects on plant growth resulting from applications of copper in fungicidal preparations, together with the general distribution of copper both in soils and in plants, have contributed to the belief that this element may be essential to plant nutrition. Definite proof of this is difficult to establish, since the minimum amount of copper required by plants now appears to be very small and, further, the accumulation of copper in seeds is shown to be very general. Earlier observations of C. B. Lipman and A. L. Sommer[43] indicated that in the absence of copper the production of flowers appeared restricted even in plants otherwise appearing normal. Further work by C. B. Lipman and G. Mackinney[44] not only confirms the failure of barley to produce seed in copper-free nutrients but suggests that copper is necessary for phases of plant growth other than flower and seed formation. In experiments with flax, tomatoes, and sunflowers by A. L. Sommer[45] extremely poor growth is recorded in the absence of copper, whereas the addition of as little as 0·06 p.p.m. produces 12—40 times as much green matter. The effect of copper deficiency does not appear in the plants until 5—7 days after the transference of seedlings to copper-free media. The suggestion is made that copper acts as an auto-oxidant in plant metabolism.

The effects of copper and other heavy metals on the growth of fungi are considered below.

Iodine. Little of importance has been added to our knowledge of relationships between iodine and plant growth. The stimulative effects recorded some years ago by O. Loew and Stoklasa have by no means received general confirmation[46, 47]; and the few papers

[41] *Phytopath.*, 1930, **20**, 967; *B.*, 269.
[42] *Bot. Gaz.*, 1930, **84**, 410; *B.*, 1930, 834. [43] *Plant Physiol.*, 1926, **1**, 231.
[44] *Ibid.*, 1931, **6**, 593; *A.*, 1201. [45] *Ibid.*, p. 339; *B.*, 733.
[46] T. von Fellenberg, *Mitt. Lebensm. Hyg.*, 1927, **18**, 253.
[47] H. Elleder, *Z. Pflanz. Düng.*, 1928, **12**, *A*, 87 : *B.*, 1928, 795.

appearing in the current year's literature report effects of an opposite character. In culture solutions as little as 1·27 p.p.m. of iodine depressed growth.[48] The more extensive researches of K. Scharrer and his co-workers [49] show that in soil cultures, iodide, iodate, and periodate of potassium injure the germination and development of cereals to extents which decrease in the order named. In water cultures similar results were obtained, the degree of injury of various salts being in the order potassium iodide >sodium iodide>aqueous iodine>potassium iodate>sodium iodate>potassium periodate> sodium periodate. Although the crop-increasing effects of iodine compounds lack adequate confirmation, the increased iodine content of crops grown with " iodised " manures [50] appears to be definitely established.[51] The significance of this point in relation to human pathology, together with a comprehensive survey of the general position of iodine in agriculture, is given by W. Gaus and R. Griessbach.[52]

Sodium. The long-standing problem of the rôle of sodium in plant nutrition is revived but not greatly clarified by the observations of P. de Sornay,[53] which indicate considerable selectivity in the assimilation of potassium and sodium among different species of plants. The sodium content of sugar-cane leaves, normally small in comparison with that of potassium, increases considerably during the early stages of ripening. With restricted phosphate supplies, the intake of sodium declines and relatively large amounts of potassium, together with iron and chlorides, accumulate in the leaves. Coconut palms even when grown at great distances from the sea accumulate large proportions of sodium chloride. O. Eckstein [54] reports beneficial effects on the growth of oats from additions of sodium salts to soils of low sodium content but high adsorptive power. In soils of low adsorptive capacity sodium salts depressed growth, presumably as a result of relatively high concentrations in the soil solution. V. Vincent and J. Herviaux [55] attach importance to the accumulation of sodium in parts of plants in which physiological activity is greatest. This accumulation is more marked in plants grown on acid soils.

Manganese. Although considerable attention has been given

[48] M. Cotton, *Bull. Torrey Bot. Club*, 1930, **57**, 127; *A.*, 537.

[49] K. Scharrer and W. Schropp, *Biochem. Z.*, 1931, **236**, 187; **239**, 74; *A.*, 1099, 1200.

[50] K. Scharrer *et al.*, *Angew. Bot.*, 1927, **9**, 187; *Naturwiss.*, 1927, **15**, 539.

[51] Von Fellenberg, *loc. cit.*

[52] *Z. Pflanz. Düng.*, 1929, **13**, *A*, 321; *B.*, 1929, 570.

[53] *Bull. Assoc. Chim. Sucr.*, 1930, **47**, 370; *B.*, 409.

[54] *Ergeb. Agrik.-chem.*, 1930, **2**, 125; *B.*, 605.

[55] *Ann. Sci. agron. franç.*, 1929, **46**, 444; *B.*, 1930, 962.

to the importance of this element in the chemistry of soils, its bearing on plant nutrition has received little examination recently. In experiments with *Chlorella*, E. F. Hopkins [56] observes that increased growth due to the presence of manganese increases with the alkalinity of the medium. The optimum concentration of the element is 1 in 5,000,000, whereas the lower toxic limit is 1 in 50,000. The function of manganese is assumed to be that of regulating the ratio of ferrous to ferric iron within the tissue. W. B. S. Bishop [57] has examined the effects of manganese at various concentrations on plant growth. Manganese is normally concerned with chlorophyll activity and carbon assimilation. Higher concentrations do not become toxic as a result of reduced iron intake. Additions of calcium counteract manganese toxicity. Further examples of the apparent association of pathological conditions with manganese deficiency are given by G. Samuel and C. S. Piper [58] in the case of speck disease in oats, by H. A. Lee and J. S. McHargue [59] with the Pahala blight of sugar cane, and by L. G. Willis [60] in the debatable question of chlorosis.

The Chemistry of Plant Juices.

There has been a considerable revival of interest in this subject consequent upon many attempts to correlate the composition of plant fluids either with the metabolic changes and distribution of various plant constituents or with external nutritional conditions. For the latter purpose, difficulties in the interpretation of results are often associated with the obvious practical difficulty of assessing differences between the contents of the rising stream of nutrient and of cell fluids containing partly or wholly metabolised materials. Meyer [61] has emphasised the fact that the nature of the soluble matter expressed from green plant tissues depends considerably on the technique employed in obtaining it, and more particularly on any form of preliminary treatment of the material which may affect its moisture content. This is further confirmed by J. D. Sayre and V. H. Morris.[62] The expressed juice from material subjected to a preliminary grinding process contained practically the same amount of sugar in the successive portions extracted. Preliminary mincing, however, resulted in a steady decline in sugar content as successive fractions were removed. The use of high pressure (5000 lb. per sq. in.), followed by pressure filtration

[56] *Science*, 1930, **72**, 609; *A.*, 400.
[57] *Australian J. Exp. Biol. Med. Sci.*, 1928, **5**, 125; *A.*, 1928, 1060.
[58] *J. Dept. Agric. S. Australia*, 1928, **31**, 696; *A.*, 1928, 1064.
[59] *Phytopath.*, 1928, **18**, 775.
[60] *N. Carolina Agric. Exp. Sta. Bull.*, 1928, No. 257; *B.*, 1929, 408.
[61] *Plant Physiol.*, 1929, **4**, 103. [62] *Ibid.*, 1931, **6**, 139; *A.*, 775.

of the expressed juice, is advocated. A serviceable press for small amounts of material is described by W. Leach.[63] Examination of the p_H and phosphate contents of expressed juices obtained at various pressures by M. M. McCool and W. J. Youden [64] indicates a steady decrease in these values with rising pressure. A further variation in technique involves the killing of the tissue by immersion in hot water prior to expression of the sap.[65] Juices so obtained have a much higher osmotic pressure than those from similar but living tissue. It is stated that this difference is not the outcome of decomposition of plant constituents resulting from the preliminary treatment.

Physical Properties.—In many respects, investigations of plant juices are still in a very undeveloped stage, and such physical characteristics as are easy of determination have, very naturally, formed the basis of much research of a pioneering character. Thus the freezing points and specific conductivities of juices from various organs of sorghum plants are measured by J. H. Martin, J. A. Harris, and I. D. Jones,[66] and the values compared at different stages of growth. It is of interest to note that under low soil moisture conditions these physical characteristics were not appreciably altered, nor was any evidence obtained of the presence of colloidally " bound " water in the juices. Among different varieties of sorghum the specific conductivity of the juices showed considerable variation, but the freezing points were not very different. Use has also been made of these physical properties in attempts to elucidate relationships between the concentration of nutrients in the soil solution and that of the plant juices. J. A. Harris and T. A. Pascoe [67] indicate a positive correlation between the freezing-point depression, specific conductivity, and sulphate content of cotton-leaf juices and the specific conductivity and soluble sulphate content of the soil.

Reaction.—Other investigators have utilised the reaction of plant saps as a basis of comparison. Changes in the p_H of nutrient media produce changes in internal sap reaction which are greater in root saps than in those of leaves.[68] In an interesting investigation R. A. Ingalls and J. W. Shive [69] find the hydrogen-ion concentration of plant juices to vary inversely with the light intensity to which the plants are exposed, differences being greater in fleshy- than in thin-leaved plants. The soluble iron content of the juices varies

[63] *Ann. Bot.*, 1931, **45**, 537; *A.*, 1201.
[64] *Contr. Boyce Thompson Inst.*, 1931, **3**, 267; *A.*, 1201.
[65] H. Walter, *Ber. deut. bot. Ges.*, 1928, **46**, 539; *A.*, 1929, 360.
[66] *J. Agric. Res.*, 1931, **42**, 57; *A.*, 775.
[67] *Ibid.*, 1930, **41**, 767; *A.*, 399.
[68] *Planta* [*Z. wiss. Biol.*], 1931, **12**, 575; *A.*, 775.
[69] *Plant Physiol.*, 1931, **6**, 103; *A.*, 775.

with the hydrogen-ion concentration. Plants whose juices are characterised by low hydrogen-ion concentrations have high total- and low soluble-iron contents, the order being reversed in juices of high hydrogen-ion concentrations. An examination of the differences in p_H of the fluids drawn from various organs of the same plant is described by J. D. Sayre [70] in the case of maize. Greatest acidity exists in the sap of sheath tissues. The buffer capacity and also the phosphate, nitrate, total nitrogen, amino-acid, and colloid contents are much greater in juices from sheath and leaf tissues than in those from the stems. From time to time it has been suggested that the reaction of plant juices is related to the extent of injury by boring and sucking insects. In the case of maize, neither p_H nor the total acidity could be correlated with infestation by the European maize borer. J. M. Robertson and A. M. Smith [71] have recorded changes in the reaction of potato tuber sap. In the dormant stage little difference exists in the distribution of acidity in various parts of the tuber. The beginning of sprouting is associated with rising acidity in areas adjacent to active eyes, this being a result of internal changes and independent of the p_H of soil. During growth the acidity of the sap increases as maturity is approached. Significant changes in p_H are associated with the incidence of disease. A similar investigation of changes in the reaction and other characteristics of the juices of French beans during various stages of growth is recorded by C. N. Acharya and B. N. Sastri.[72] The reaction and buffer system of plant juices are examined by C. T. Ingold,[73] who stresses the importance of the carbon dioxide present, not only in actual determinations of p_H values but in the more general consideration of composition and physiological activities. In the sap of potato tubers the principal buffer agents are the citrates, malates, and phosphates present, the effects of proteins, asparagine, and oxalates being of surprisingly little significance in this respect. The buffer index (β) of saps may be represented as the summation of the indices of all the single buffer systems present over any given range. The β-curves are U-shaped, and to their form, proteins and amino-acids contribute very little. S. H. Martin and co-workers,[74] in a series of papers dealing with sunflower and other plants, arrive at similar conclusions.

Inorganic Constituents.—Changes in the base contents of saps with growth have been examined, in most cases with a view to

[70] *Ohio Agric. Exp. Sta. Bull.*, 1930, No. 446, 38; *A.*, 399.
[71] *Biochem. J.*, 1931, **25**, 763; *A.*, 1102.
[72] *J. Indian Inst. Sci.*, 1931, **14**, *A*, 1; *A.*, 1102.
[73] *Protoplasma*, 1930, **9**, 441, 447, 456; *A.*, 272.
[74] *Ibid.*, 1927, **1**, 497, 522; **2**, 45; 1928, **3**, 273, 282; *A.*, 1928, 92, 1406.

correlation with corresponding concentrations in nutrient media. Thus the nitrate content of the sap of maize is observed by N. A. Pettinger [75] to be closely correlated with that of the soil bearing the plant, and the phosphate content of the sap with the amount of fertiliser applied. There is also a somewhat obscure but nevertheless definite proportionality between the brown coloration of the clarified press juice and the available potash content of the soil. These relationships are considered sufficiently rigid to permit the utilisation of sap analyses as indications of the nutrient status of soils. The p_H of the saps examined is closely correlated with amounts of potash fertiliser applied to the soil but not with the initial potassium content of the soil. M. M. McCool and M. D. Weldon [76] examined the saps of a number of agricultural crops and observed a general relationship between the concentration of individual ions in the saps and the proportions of these added to soil in the form of fertilisers. A deficiency of any one essential nutrient such as would reduce the growth rate of the plant is followed by an abnormally high accumulation of other nutrients in the sap. The subsequent addition to the soil of the deficient element tends to bring the concentration of all nutrients in the sap to a normal proportion. An interesting observation is reported by E. Canals, J. Canayé, and E. Cabanes,[77] who show that sodium, potassium, magnesium, and phosphates present in plant juices are almost entirely dialysable, whereas calcium in nearly all cases is in a non-dialysable form. Indications of a process akin to base exchange between kations in nutrient solutions and those in plant saps are given by P. Genaud,[78] who examined the press juices of cells after exposure to solutions of electrolytes. Equilibrium between kations within and without the cells is reached in accordance with the law of mass action. Results of a similar character are obtained by W. C. Cooper and W. J. V. Osterhout.[79] The intake of ammonia by *Valonia* is followed by p_H changes in the sap and a depletion of potassium.

Formation and Distribution of Certain Plant Constituents.

Nitrogen Compounds.—Growing interest in the nitrate-reducing powers of the roots of various species of plants is exemplified by the work of W. Dittrich,[80] who suggests a system of plant classification based on the capacity for nitrate accumulation. The reduc-

[75] *J. Agric. Res.*, 1931, **43**, 95; *B.*, 1111.
[76] *J. Amer. Soc. Agron.*, 1928, **20**, 778; *B.*, 1929, 106.
[77] *Bull. Soc. Chim. biol.*, 1930, **12**, 1022; *A.*, 1930, 1482.
[78] *Rev. gén. Colloïd.*, 1930, **8**, 241; *A.*, 1930, 1482.
[79] *J. Gen. Physiol.*, 1930, **14**, 117; *A.*, 1930, 1483.
[80] *Planta* [*Z. wiss. Biol.*], 1930, **12**, 69; *A.*, 130.

tion of nitrates is ascribed to enzymic action and as such is largely controlled by the p_H of the plant sap. Optimum reducing power is associated with p_H 7·6 in the sap. Marked differences exist between the reducing power of stem saps and those of roots and leaves. Nitrate-accumulating plants utilise this form of stored nitrogen when external supplies are exhausted, *e.g.*, when grown in media containing carbohydrates only.

Numerous investigations of the distribution of the nitrogen of plants under various conditions of growth have appeared. The translocation of nitrogen and the rates of synthesis or decomposition of protein within the plant are largely controlled by the water present in the tissues. According to K. Mothes [81] a deficiency of water induces protein decomposition and reduced carbon dioxide production in older leaves and simultaneously a synthesis of protein and increased respiration in younger leaves. Under these conditions the younger portions of the plant would appear to continue their growth at the expense of the older portions.

Much interest centres round nitrogenous changes in fruit trees. A. S. Mulay [82] records a winter accumulation of nitrogen in the bark of Bartlett pear shoots, falling steadily during the growth period and recurring as the dormant season approaches. These changes fall mainly on the insoluble nitrogen fraction. Corresponding changes occur in the total nitrogen of the woody tissues, but here the soluble nitrogen is mainly concerned in the fluctuations. The soluble protein, which forms 6—12% of the total nitrogen of the bark, accumulates towards autumn and decreases again as spring approaches. In the wood, similar variations occur, although the soluble proteins are present in smaller proportions than in the bark. Potter [83] and his colleagues in New Hampshire have made somewhat similar investigations with apple spurs, with special reference to conditions coincident with fruit bud formation. In fruiting spurs the total nitrogen is higher and starch content lower than in non-fruiting spurs. Fruit bud formation is associated with an accumulation of insoluble nitrogen and a lowered proportion of soluble carbohydrate. The association of shoot production with stem areas containing accumulations of nitrogen is shown also by P. A. Davies,[84] who finds that cuttings of *Salix nigra* develop roots from stem areas of low nitrogen content and shoots from those of high nitrogen content.

[81] *Planta* [*Z. wiss. Biol.*], 1931, **12**, 686; *A.*, 660.

[82] *Plant Physiol.*, 1931, **6**, 333, 519; *A.*, 990, 1197.

[83] G. F. Potter, H. R. Kraybill, S. W. Wentworth, J. T. Sullivan, and P. T. Blood, *New Hamps. Agric. Exp. Sta. Tech. Bull.*, 1930, No. 41; *A.*, 400; G. F. Potter and T. G. Phillips, *ibid.*, No. 42; *A.*, 400.

[84] *Bot. Gaz.*, 1931, **91**, 320; *A.*, 883.

Reference should be made to a very thorough examination of both nitrogenous and mineral constituents of the oat plant from the seedling stage to maturity by T. W. Fagan and J. E. Watkin [85]; and also to papers by M. Steiner and H. Löffler [86] on the distribution of ammonia and volatile amines in various plants, and by G. M. Armstrong and W. R. Albert,[87] on the effect of fertilisers on the nitrogen distribution in cotton.

Carbohydrates.—Seasonal variations of the carbohydrate distribution in plants have again formed the subject of a number of investigations. In the roots of *Geum urbanum*, J. Cheymol [88] records accumulations of mono- and di-saccharides, hydrolysable by emulsin, during periods of reduced chlorophyll activity, of polysaccharides in proportion to the vegetative activity of the plant, and of geoside, which occur mainly in the spring. Storage of carbohydrates in stem bases in dormant periods is also recorded in the case of *Stipa pulchra* by A. W. Sampson and E. C. McCarty,[89] together with significant data of carbohydrate metabolism bearing on the system of intensive grazing. Thus, regenerative growth following cutting or grazing leads to utilisation of the carbohydrate reserves. In the younger stages of growth, cutting does not seriously reduce the final accumulation of carbohydrate when vegetative growth ceases, but if cutting is delayed until after the flowering stage, the maximum carbohydrate storage for the dormant season is not developed and reduced growth in the ensuing season may result. The association of rapid growth in trees with the appearance of relatively high proportions of reducing substances is referred to in an examination of sugar prunes by L. D. Davis.[90] In a comparison of bearing and disbudded trees during periods of active growth, the former were characterised by high proportions of reducing substances and low starch contents in the aerial parts and low starch contents in the roots.

A series of papers by M. Samec and colleagues [91] makes a notable addition to the chemistry of starches. Characteristic differences between amylo- and erythro-substances are examined. In sols obtained by boiling potato starch with water under pressure, amylo-substances are the more strongly absorbed by cotton. The viscosity of amylo-sols increases fairly rapidly with rise of temper-

[85] *Welsh J. Agric.*, 1931, **7**, 229; *A.*, 1339.
[86] *Jahrb. wiss. Bot.*, 1929, **21**, 463; *A.*, 1931, 990.
[87] *J. Agric. Res.*, 1931, **42**, 689; *B.*, 775.
[88] *Bull. Soc. Chim. biol.*, 1931, **13**, 470; *A.*, 883.
[89] *Hilgardia*, 1930, **5**, 61; *A.*, 660.
[90] *Ibid.*, 1931, **5**, 119; *A.*, 1339.
[91] [With E. Pehani], *Kolloidchem. Beih.*, 1931, **33**, 103; *A.*, 941; [with R. Klemen], *ibid.*, p. 254; *A.*, 1198; [with D. Andrié], *ibid.*, p. 269; *A.*, 1124.

ature, and is considerably altered by the presence of neutral salts. Erythro-sols, under these conditions, are but little affected; but are the more readily hydrolysed by acids and by hydrogen peroxide. Amylo-substances are concluded to be more highly associated and hydrated and to carry greater electric charges than erythro-substances. Amylo-pectins obtained by the fractional dissolution of starches are shown to contain fatty acids, and may be used in conjunction with data of *X*-ray spectra as a basis for a general classification of starches into two groups typified by potato and wheat starches. The migration velocities of the constituents of potato starch are in the order amylo-pectin>amylose>erythro-amylose.

In a later paper[92] the isolation of starch derivatives of high phosphate content is described. One of these appeared, from its molecular weight and phosphorus content, to be of intermediate composition between a compound of 1 molecule of phosphoric acid with a di- and a tri-saccharide. The neutralisation curve of this substance exhibits two discontinuities resembling those of phosphoric acid itself. The isolation of this compound(?) has a significant bearing on the nature of "phytovitellin" previously recorded.[93] Phytovitellin contains both nitrogen and phosphorus associated with the polysaccharide and linked with it through the phosphorus radical. This combination appears weaker in wheat than in potato starch. Preferential removal from wheat starch of nitrogen with respect to phosphorus by alkali leaves a residue exhibiting properties similar to those of potato starch and containing electrochemically active phosphorus. Further treatment with hot water removes a substance containing phosphorus, and the starch reverts to the wheat type.

The nature of hemicelluloses has been examined by I. A. Preece[94] and by E. Anderson.[95] The former author concludes that free hemicellulose is a simple urono-xylan, while the latter assumes the existence of a second type of hemicellulose yielding aldobionic acid on hydrolysis, thus resembling the plant gums. A general survey of the chemistry of hemicelluloses is given by S. A. Waksman and R. A. Diehm[96] in an introduction to an extensive investigation of the decomposition of these substances by micro-organisms.

The distribution of lignin in woody tissues, examined after

[92] M. Samec [with S. Seliskar and V. Zitko], *Kolloidchem. Beih.*, 1931, **33**, 449; *A.*, 1277.

[93] M. Samec [with W. Bendger], *ibid.*, p. 95; *A.*, 941.

[94] *Biochem. J.*, 1931, **25**, 1304; *A.*, 1198.

[95] *J. Biol. Chem.*, 1931, **91**, 559; *A.*, 884.

[96] *Soil Sci.*, 1931, **32**, 73, 97, 119; *A.*, 1192.

removal of cellulosic material, appears to vary in woods of different types. From hardwoods the lignin residue consists only of the middle lamella, whereas that from soft woods contains secondary layers in addition.[97] In jarrah wood, H. E. Dadswell[98] describes the lignin as occurring in fine radial lines in the cell walls. His work further suggests that chemical combination of cellulose and lignin in wood cells is unlikely. The possibility that a high lignin content in wheat straw is conducive to lodging by causing extreme brittleness is suggested by J. Davidson and M. Phillips.[99]

In a suggestive investigation[1] of lignins from a variety of plants, relationships are suggested between the botanical origin of lignins and the position of the principal maximum in their ultra-violet absorption spectra. Such spectroscopic evidence confirms the presence in lignin of partially methylated di- and tri-hydric phenol groups.

Further optical investigations of wood fibres by K. Freudenberg, F. Sohns, W. Dürr, and C. Niemann[2] lead to the assumption that two stages occur in the formation of lignin, *viz.*, (1) the condensation of many (probably 12) molecules of hydrated γ-3 : 4-dihydroxyphenyl-$\alpha\beta$-propylene glycol to form a chain in which the free phenolic groups may be methylated, and (2) condensation or polymerisation of these chains into larger aggregates by chemical action or possibly as a *post-mortem* process.

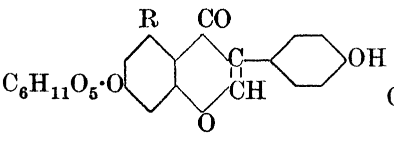
Glucosides.—Several new glucosides have been isolated and described, and further investigations are recorded of the structure of others already known. From *Salix purpurea*, C. Charaux and J. Rabaté[3] have obtained the β-glucoside, salipurposide, m. p. 227°, a monoglucoside, $C_{21}H_{22}O_{10}$, yielding on hydrolysis dextrose and the phenol, salipurpol, $C_{15}H_{12}O_5$.

Salireposide,[4] m. p. 206°, has been obtained from the bark of *Salix repens*. Hydrolysis with dilute acid yields dextrose, benzyl alcohol, and an unknown phenol.

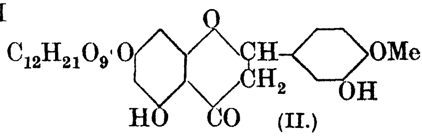
Gaultherioside, isolated from *Gaultheria procumbens*,[5] is hydrolysed to dextrose, xylose, and ethyl alcohol. It is not hydrolysed by rhamnodiastase. From black alder bark, M. Bridel and C. Charaux[6]

[97] W. M. Harlow, *Ind. Eng. Chem.*, 1931, **23**, 419; *A.*, 883.
[98] *J. Counc. Sci. Ind. Res. Australia*, 1931, **4**, 185; *A.*, 1339.
[99] *Science*, 1930, **72**, 401; *A.*, 537.
[1] R. O. Hertzog and A. Hillmar, *Ber.*, 1931, **64**, [*B*], 1288; *A.*, 942.
[2] *Cellulosechem.*, 1931, **12**, 263; *A.*, 1278.
[3] *Compt. rend.*, 1931, **192**, 1478; *A.*, 1199; *Bull. Soc. Chim. biol.*, 1931, **13**, 590, 814; *A.*, 1100, 1341.
[4] N. Wattiez, *Bull. Soc. Chim. biol.*, 1931, **13**, 658; *A.*, 1100.
[5] J. Rabaté and S. Rabaté, *ibid.*, p. 604; *A.*, 1100.
[6] *Compt. rend.*, 1930, **191**, 1151, 1374; 1931, **192**, 1269; *A.*, 131, 274, 885.

prepared frangularoside, $C_{21}H_{20}O_9$, a rhamnoside yielding an unknown product, frangularol, on hydrolysis. Frangularoside in the bark exists in a form of combination from which it is liberated by an enzyme present in the bark. The parent substance, on hydrolysis with acid, yields a considerable proportion of emodol, and with yeast, 1 molecule of frangularoside to 2 molecules of dextrose. E. Walz [7] publishes an extensive examination of some glucosides of the soya bean, from which genistin, daidzin, and three saponin-glucosides were obtained. To genistin, from which dextrose and genistein are produced on hydrolysis, is ascribed the formula (I),



(I.)



(II.)

daidzin having a similar formula with R = H.

The three saponin-glucosides (aglucones) are characterised by the presence of both pentose and dextrose residues, accompanied by flavone derivatives. It is probable that one of these is a hydroxymethyl derivative of 8-hydroxy*iso*flavone.

Further investigations of natural glucosides by A. Robertson [8] and colleagues have elucidated the structure of hesperidin, to which is assigned the formula (II).

In an interesting paper A. Cugnac [9] shows that the glucosides of European *Gramineæ* are principally of the lævulosan type whereas those of warmer climates contain sucrosans. The lævulosans occur in the stems and tend to accumulate in the roots, particularly in later season of growth.

Organic Acids.—Among investigations of the distribution of the simpler organic acids of plant materials, should be mentioned those of Nelson and his colleagues, who have examined the common cereals and a number of vegetables.[10] Oxalic, citric, and malic acids are common to the vegetable plants. Wheat, barley, maize, oats, and rye all contain aconitic, malic, citric, and small amounts of oxalic acid and in addition malonic acid is found in wheat, barley, and oats, and tricarballylic acid in barley and maize. The presence and function of oxalates in seeds and fruits is the subject of a series of papers by A. Niethammer, in whose view the separation of

[7] *Annalen*, 1931, **489**, 118; *A.*, 1304.

[8] F. E. King and A. Robertson, *J.*, 1931, 1704; *A.*, 1040.

[9] *Bull. Soc. Chim. biol.*, 1931, **13**, 125; *A.*, 661.

[10] E. K. Nelson and H. Hasselbring, *J. Amer. Chem. Soc.*, 1931, **53**, 1040; *A.*, 661; E. K. Nelson and H. H. Mottern, *ibid.*, pp. 1909, 3046; *A.*, 884, 1199.

calcium oxalate crystals in fruit cells results from the presence of carbonaceous material in excess of immediate requirements and is a temporary storage phenomenon rather than the deposition of unutilisable material. The crystals gradually disappear as the fruit ripens and with this disappearance there is associated the formation of acetaldehyde.[11] This temporary formation of calcium oxalate is observed in a wide range of fruits and seeds.[12, 13]

Aluminium.—It is convenient here to consider the question of the presence of aluminium in plants. Much has been written of the relationship between soil acidity and the injurious effects of aluminium on plant growth, but considerable difference of opinion exists as to whether acid soil injury is entirely attributable to the presence of soluble aluminium. It is now shown [14] that in water cultures lettuce can withstand considerable changes in acidity (p_H 7·5—3·2) without appreciable injury, whereas the presence of extremely small amounts of aluminium has a marked inhibitory effect. Barley yields in soils, however, are closely correlated with the amount of " active " aluminium present.[15] The susceptibility of different species of plants to aluminium poisoning varies considerably and in many cases a highly acid medium is not a necessary condition for aluminium injury.[16]

More recently the position of aluminium as a normal constituent of plants has received attention. In the early work of Burgess and Pember [17] an accumulation of aluminium in roots and leaves of acid-soil plants was observed and little appeared in the stems. Other investigators record similar observations.[18, 19] G. Bertrand and G. Levy [20] have traced variations in the aluminium contents of a number of edible roots with age. Greatest accumulations of aluminium occur in leaves, those of spinach, rhubarb, and radish being particularly rich in this element (100—280 mg. per. kilog. dry weight). A detailed examination of the leaves of mulberry grown on various types of soil indicates considerable quantities of alu-

[11] *Planta* [*Z. wiss. Biol.*], 1930, **12**, 53, 399; *A.*, 133, 537; *Biochem. Z.*, 1930, **227**, 462; *A.*, 133.

[12] *Z. Unters. Lebensm.*, 1931, **61**, 103, 217; *A.*, 885.

[13] J. Greger, *Planta* [*Z. wiss. Biol.*], 1930, **12**, 49; *A.*, 133.

[14] B. E. Gilbert and F. R. Pember, *Soil Sci.*, 1931, **31**, 267; *B.*, 604.

[15] Burgess and Pember, *Rhode I. Agric. Exp. Sta. Bull.*, 1923, No. 194.

[16] F. T. McClean and B. E. Gilbert, *Soil Sci.*, 1927, **24**, 163; *B.*, 1927, 855; *Plant Physiol.*, 1928, **3**, 293.

[17] *Loc. cit.*

[18] E. V. McCollum, O. R. Rask, and J. E. Becker, *J. Biol. Chem.*, 1928, **77**, 753; 1930, **85**, 779; *A.*, 1928, 793; 1930, 492.

[19] L. Kahlenberg and J. O. Cloes, *ibid.*, 1929, **83**, 261; 1930, **85**, 783; *A.*, 1929, 1098; 1930, 492.

[20] *Compt. rend.*, 1931, **192**, 525; *A.*, 662.

minium in the intracellular juices in all cases, stems, bark, and leaf veins having higher proportions than the soft leaf tissues. It is considered unlikely that aluminium can enter the plant in such quantities as were observed and be deposited in the tissues without being concerned in some at least of the metabolic processes of the plants.[21]

Nutrition and Composition of Plants as related to the Incidence and Control of Diseases.

The steadily increasing interest in the control of plant diseases, both by direct application of chemical poisons and indirectly by the elimination of predisposing causes due to faulty nutrition, has resulted in the publication of numerous investigations on this subject. The majority of these are more properly considered from the agricultural point of view. However, since the more purely biochemical aspects of these problems are becoming increasingly apparent, certain typical investigations seem suited for inclusion here. Nutritional factors have been shown to play an important part in the spread of " wildfire " in tobacco.[22] As has been noted in a number of instances, the greatest predisposing causes are a deficiency of potash and a relative excess of nitrogen. The effect of phosphates seems much less definite. A deficiency appears to increase the plant's susceptibility but, on the other hand, generous applications of phosphatic manures do not produce a correspondingly increased resistance. In this case soil reaction was a relatively unimportant factor. The existence of such relationships is also indicated by investigations from a rather different point of view. In many cases diseased plants contain significantly different proportions of mineral and other constituents from normal plants. Thus palms, infected with " decline " disease, have lowered contents of nitrogen, phosphorus, and potassium, higher calcium, and less carbohydrates than healthy specimens. It is significant that the proportions of the " secondary " nutrients sodium, magnesium, sulphur, and chlorine are not appreciably affected by disease, and, moreover, the recognised treatment (addition of copper sulphate to the soil) results in changes in composition tending to approach the normal.[23] Similarly, tobacco plants infected with mosaic disease contain smaller proportions of reducing sugars, disaccharides, starches, and pentosans than healthy plants.[24] Investigations of

[21] D. Ongaro, *Atti R. Accad. Lincei*, 1931, [vi], **13**, 202; *A.*, 1200.

[22] K. Böning, *Z. Parasitenk* [*Z. wiss. Biol.*], 1930, **2**, 645; *A.*, 133.

[23] A. R. C. Haas and L. J. Klotz, *Hilgardia*, 1931, **5**, 511; *A.*, 1201.

[24] A. A. Dunlap, *Amer. J. Bot.*, 1931, **18**, 328; *A.*, 886; compare *Ann. Reports*, 1930, **27**, 240.

spike disease reported last year [25] have been extended to *Dodonœa viscosa* by B. N. Sastri and N. Narayana, who record that diseased plants are characterised by increased contents of sugars and starches and lowered amounts of calcium.[26]

Problems concerning the effects of fungicides and insecticides on plant growth and composition are tending to indicate in no uncertain manner the need for an extension of the scope of fundamental research to cover the conditions obtaining in the field application of these poisons. A prominent instance appears in connexion with the use of petroleum oils in insecticides. Injury to plant foliage and fruit from these oils is not always outwardly visible, nor is the immediate cause of the injury understood. The many attempts to correlate physical and chemical properties of oils with their injurious action seem doomed to failure unless more definitely biochemical facts are made clear. Oil injury to foliage bears some relationship to respiratory activity. The work of J. Green and A. H. Johnson [27] indicates that oils having more than 16% of sulphonatable matter increase, and those with less than 16% decrease, respiratory rates of bean leaves. V. W. Kelley,[28] however, working on deciduous fruit trees, finds that all petroleum oils, irrespective of the degree of purification, reduce respiration rates. The effect is mainly confined to the under surface of leaves and is greater in old than in young leaves. A general discussion of the effects of various grades of oils on the growth of plants is given by C. W. Woodworth.[29]

Biochemistry of Moulds.

The widespread interest in the growth and metabolism of moulds, which in late years has received such an impetus from the developments in fermentation industries, has again been maintained during the year under review.

Nutrition.—The apparent selectivity in the assimilation of nitrogenous foods already noted in the case of the higher plants finds its counterpart in the case of moulds. In culture solutions *Aspergillus oryzœ* [30] can utilise either nitrates or ammonium salts or both simultaneously. A predominance of ammonium salts results in retarded growth and the medium becomes increasingly acid. The addition of phosphates minimises reaction changes and growth is

[25] *Ann. Reports*, 1930, **27**, 239.
[26] *J. Indian Inst. Sci.*, 1930, **13**, *A*, 147; *A.*, 537.
[27] *Plant Physiol.*, 1931, **6**, 149; *A.*, 774.
[28] *Illinois Agric. Exp. Sta. Bull.*, 1930, No. 353, 581; *A.*, 1339.
[29] *J. Econ. Entom.*, 1930, **23**, 848; *B.*, 268.
[30] T. Sakamura, *Planta* [*Z. wiss. Biol.*], 1930, **11**, 765; *A.*, 125.

improved. Absorption of nitrate-nitrogen tends to maintain a constant p_H in the medium and both growth and nitrogen intake are high. The form of nitrogen utilised is also affected by the nature of other constituents, notably the carbohydrates. Nitrate absorption is favoured by sugars in the order lævulose>sucrose>dextrose. Reaction changes in the medium associated with the assimilation of different forms of nitrogen vary with different species of fungus. F. Labrousse[31] shows that *Cladosporium cucumerinum* and *Verticillium dahliæ* utilise ammonium nitrate and sulphate and produce an immediate acid reaction, but with calcium nitrite an immediate alkaline reaction results. With *Sclerotinia libertiana* and *S. minor*, the media become increasingly acid as growth proceeds. An extensive and general investigation of this aspect of fungal nutrition is given by K. Rippel.[32] The enzyme activity of fungi is frequently influenced by the supply of nutrients. G. von Doby and E. Fehér[33] showed that the production of mycelium of *Penicillium* was but little affected by the absence of calcium, but was markedly depressed if magnesium was omitted and ceased entirely in the absence of phosphates. The increased invertase production resulting from the addition of sugar to the medium was normal in the absence of calcium or with a moderately reduced phosphate supply, but was reversed where magnesium was absent or where the phosphate concentration was small. The optimum p_H of the medium for invertase production was not, however, appreciably affected by the nature of the nutrient salts used.

Effects of Heavy-metal Salts.—Metz[34] has shown that the effects of copper, zinc, and iron salts on the growth, pigmentation, and spore production were of a general character for a number of species of fungus, although minor varietal differences in the p_H, ammonia, and sugar contents of the media are apparent. *Aspergillus niger* is reported by W. Schwartz and H. Steinhart[35] to take up a more or less definite amount of copper in the early stages of growth, at a rate which is practically independent of the concentration of copper in the medium. This copper intake probably represents a definite metabolic requirement. Stimulative effects of copper, zinc, and manganese on the growth of *Aspergillus flavus* and *Rhizopus nigricans* are examined by J. S. McHargue and R. K. Calfee,[36] optimum effects being obtained with concentrations of 5·0, 1·0, and

[31] *Compt. rend.*, 1931, **192**, 980; *A.*, 768.
[32] *Arch. Mikrobiol.*, 1931, **2**, 72; *A.*, 1333.
[33] *Z. physiol. Chem.*, 1931, **196**, 89; *A.*, 876.
[34] *Arch. Mikrobiol.*, 1930, **1**, 197; *A.*, 1094.
[35] *Arch. Mikrobiol.*, 1931, **2**, 261; *A.*, 1334.
[36] *Bot. Gaz.*, 1931, **91**, 183; *A.*, 876.

2·5 p.p.m. of the respective metals. In mixtures of these metals the stimulatory action is shown to be an additive function. All metals increase the fat and decrease the nitrogen content of the mycelium. The assimilation of mineral nutrients by *Aspergillus* is increased by copper and zinc and decreased by manganese.

Tannase.—The ability to utilise tannin as a sole source of carbon is shown only by *Penicillium citromyces* and *Aspergillus*, among many species examined by A. Rippel and J. Keseling.[37] The production of tannase takes place only in the presence of tannin, but is not associated with the power of utilisation of tannin by the fungus. Earlier observations of Nierenstein, that the amount of gallic acid obtained from gallotannin by means of tannase preparations was less than the theoretical proportion, are now explained [38] by the fact that *A. niger* contains, in addition to tannase, a pyrogallase which destroys gallic acid. The same organism grown on a dextrose–peptone medium is also shown to produce a guanidase bringing about the quantitative decomposition of guanidine to urea and ammonia.[39]

Production of Organic Acids by Fungi.—Factors controlling the production of fatty acids by *A. niger* are examined by C. Pontillon.[40] The total production of fatty acids is approximately the same in neutral and in slightly alkaline media, but decreases somewhat in acid media. The molecular weight of the acids produced is practically independent of the reaction of the medium, but reaches a minimum at the period of fructification. The iodine value of the acids produced averages 30 in neutral media, and is slightly greater in acid conditions. The suggestion of Challenger and others that saccharic acid is an intermediate product in the conversion of dextrose and gluconic acid into citric acid by *A. niger* is now negatived by K. Bernhauer and H. Siebenäuger [41] after examination of numerous strains of this organism. Further, when *A. niger* is grown on sucrose media with minimal amounts of ammonium nitrate, evidence is advanced by Molliard [42] indicating that citric and gluconic acids are distinct oxidation products of the sugar, citric acid not being produced from gluconic acid. Oxalic acid is not formed unless sodium gluconate or acetate is added to the medium, and in these circumstances it is considered to be a definite excretion product. Citric acid production as a function of the reaction of the medium

[37] *Arch. Mikrobiol.*, 1930, **1**, 60; *A.*, 1094.
[38] *Biochem. J.*, 1931, **25**, 752; *A.*, 983.
[39] N. N. Ivanov and A. N. Aretissova, *Biochem. Z.*, 1931, **231**, 67; *A.*, 524.
[40] *Compt. rend.*, 1930, **191**, 1148; *A.*, 125.
[41] *Biochem. Z.*, 1931, **230**, 466; *A.*, 524.
[42] *Compt. rend.*, 1931, **192**, 313; *A.*, 524.

is examined by A. Frey.[43] In *Citromyces glaber* citric acid formation is optimal at p_H 3—4 and is inhibited at p_H 2. In *A. niger*, optimum production occurs at p_H 2. In both cases addition of calcium carbonate to produce p_H 3—4 favours the production of the acid. Further neutralisation to produce p_H 6·0 increases the formation of gluconic acid from *A. niger*. In various acetate media *Penicillium* (sp. ?) produces succinic, fumaric, oxalic, *l*-malic, and citric acids, the nature and quantity of the acids varying with the particular acetate provided. Alkali-metal salts favour the formation of citric and probably of oxalic acids. The suggested [44] mechanism of the production of citric acid from sugars involves the following steps : pyruvic acid and acetaldehyde ⟶ ethyl alcohol ⟶ acetic acid ⟶ succinic ⟶ fumaric ⟶ *l*-malic acids. A parallel examination of the action of *A. niger* by K. Bernhauer and H. Siebenäuger [45] indicates a yield of 16% of citric acid on the acetate destroyed. Ethyl alcohol, fumaric, malic, and glycollic acids are all converted into citric acid. The production of kojic acid from trioses is examined by F. Challenger, L. Klein, and T. K. Walker.[46] Evidence supports the conception that the formation of the acid from pentoses and hexoses occurs *via* the intermediate breakdown to triose, followed by direct condensation to kojic acid. The production of two new acids by *Penicillium glaucum* on sucrose media is reported by N. Wijkman,[47] *viz.*, glauconic acid 1, $C_{18}H_{20}O_7$, m. p. 202°, probably containing one or more lactone rings, and glauconic acid 2, $C_{18}H_{20}O_6$, probably tetrabasic.

A. G. Pollard.
J. Pryde.

[43] *Arch. Mikrobiol.*, 1931, **2**, 272; *A.*, 1333.
[44] T. Chrzaszcz and D. Tiukov, *Biochem. Z.*, 1930, **229**, 343; *A.*, 394.
[45] *Ibid.*, 1931, **240**, 232; *A.*, 1333.
[46] *J.*, 1931, 16; *A.*, 525.
[47] *Annalen*, 1931, **485**, 61; *A.*, 523.

CRYSTALLOGRAPHY.

THE past two years have seen a rapid extension of the well-tried methods of crystal-structure analysis over the whole field of chemistry, and even beyond it into biological questions. In the metrical structural chemistry of the future it will take its place with the study of spectra and the optical and magnetic properties of molecules. Already the systematic inorganic chemistry, particularly for metallic substances, salts, and silicates, needs to be rewritten round the data supplied by crystal analysis. At the same time crystal physics has increasingly succeeded in correlating physical properties with crystal structure, and structure with fundamental quantum mechanical relations.

An important landmark is the publication of the *Strukturbericht* of the *Zeitschrift für Kristallographie.* Professor P. P. Ewald and C. Hermann have produced a model of a book of reference. It contains in its 800 pages practically all the relevant data that had appeared in crystal structural work up to the end of 1928. The arrangement is simple and facilitates reference. It is partly geometrical and partly chemical. Substances are classified in the following sections: A, elements; B, compounds of type AX; C, AX_2; D, A_mX_n; F, $A_m(XY)_n$ or $A_m(XYZ)_n$; G, $A_m(BX_3)_n$; H_1, $A_m(BX_4)_n$; H_2, $A_m(BX_k)_n$. Then follow: other inorganic compounds; L, alloys; O, organic compounds.

In each section are given, first, detailed descriptions of well-established crystal types, all on a uniform plan with diagrams, not only of the crystal but of the atomic neighbourhoods, together with numerical data on all crystals of that type. Next follow critical abstracts of all papers on substances belonging to the section, whether they belong to the recognised types or not. The uniformity of the treatment of the very heterogeneous material is of great value, as it enables systematic relations to be seen much more easily than from reading original papers. The only criticism that might be made is that—inevitably, at the time the work was started—the basis of classification was not as satisfactory as the present systems based on crystal chemistry. Metallic compounds are found, for instance, scattered through many of the classes, and the relations between the different silicate structures are concealed. This would be of little importance if the very existence of the Strukturbericht did not tend to make the type symbols, *e.g.*, B_1 for sodium chloride, H_{11} for spinel, etc., pass into general use.

Wyckoff's second edition of his " Structure of Crystals " gives us an up-to-date English text-book of the subject which has been badly needed. The first part deals with the technique of the analysis of crystals and contains adequate and critical descriptions of the chief methods used. It would have been better if the arrangement of the first edition had not been so closely followed. The second part, dealing with the results of structure analysis, is admirable. No detail is attempted, but the essential features of every important structure are brought out and emphasised by clear and beautiful drawings. The complete bibliography up to the end of 1930 is also very valuable.

The second edition of Wyckoff's " Analytical Expression of the Results of the Theory of Space Groups " contains some useful perspective drawings of symmetry elements. Meyer and Mark's " Der Aufbau der Hochpolymeren Organischen Naturstoffe " is reviewed in another section of this report.

Nomenclature of Space Groups.—In 1930 a committee of the International Congress (see *Ann. Reports*, 1929, **26**, 276) met in Zurich.[1] Here it was decided to set in hand the preparation of International Tables for Crystal Structure and to arrange for the publication of standard abstracts according to the recommendation of a sub-committee.[2] For both these purposes an agreed notation for symmetry elements, crystal classes, and space groups was needed. The committee finally agreed on the Hermann–Mauguin notation. This is a rational system of notation put forward in principle by C. Hermann [3] and subsequently simplified by Ch. Mauguin.[4] As it is likely to be widely if not universally used in the future, the following brief account of it is given.

In this notation the minimum elements of symmetry needed to develop the group are directly symbolised instead of being enumerated as in older systems. In each symbol the first place is taken by a capital letter standing for the lattice type : P stands for a primitive lattice, A, B, C for lattices face-centred on the (100), (010), (001) face respectively, I for body- (inner) centred, and F for face-centred lattices. The rhombohedral lattice is designated by R, and the hexagonal by C or H according as the crystallographic axes coincide with or are perpendicular to the primitive translations of the lattice. Next follows the notation for the elements of symmetry : 1, 2, 3, 4, 6 for axes of simple rotation; $\bar{1}$, $\bar{3}$, $\bar{4}$, $\bar{6}$ for axes of rotation-inversion; and 2_1; 3_1, 3_2; 4_1, 4_2, 4_3; 6_1, 6_2, 6_3, 6_4, 6_5

[1] *Z. Krist.*, 1930, **75**, 159.
[2] J. D. Bernal, P. P. Ewald, and C. Mauguin, *ibid.*, 1931, **79**, 495.
[3] *Ibid.*, 1928, **68**, 257; 1929, **69**, 226, 250, 533; 1931, **76**, 559.
[4] *Ibid.*, p. 529.

for screw axes. 1 indicates asymmetry, $\bar{1}$ a centre of symmetry; $\bar{2}$ would indicate a symmetry plane, but owing to their special importance planes of symmetry are designated by letters: *m* stands for a reflexion plane, other letters for glide planes, *a*, *b*, *c* for glide planes with $\frac{1}{2}$ translation parallel to the *a*, *b*, *c* axes, *n* and *d* for one with $\frac{1}{2}$ or $\frac{1}{4}$ translation respectively, parallel to [011], [101], or [110].

The symmetry of any space group can be designated in terms of these elements only by using an invariable order. First comes the lattice symbol *P*, *A*, *B*, *C*, *I*, *F*, *R*, or *H*; next follows the symbol of the principal axis (except in the orthorhombic holoaxial class, where the arbitrary order *a*, *b*, *c* is followed, and in the holohedral class, where plane symbols are used instead). If there is a plane of symmetry perpendicular to this axis, it follows it immediately, separated by an oblique rule /, *e.g.*, $2/m$ for monoclinic holohedry. Next follow the secondary axes or planes with the convention that an axis symbol is only put when there is no corresponding plane perpendicular to it. Thus the holohedral classes are designated by: $C_i - \bar{1}$, $C_{2h} - 2/m$, $V_h - mmm$, $D_{4h} - 4/mmm$, $D_{3h} - \bar{3}m$, $D_{6h} - 6/mmm$, $O_h - m3m$ (the cubic system is always characterised by 3 in the second place).

The different space groups of any crystal class are distinguished by the different notations for glide planes and screw axes.

The great advantage of this notation is that each space group symbol gives all its symmetry elements without recourse to memory or tables. It is particularly valuable to *X*-ray workers, because by the use of a few simple rules the space group symbol can be written down direct from observed absent reflexions, and from the symbol the co-ordinates of the equivalent points can be written down.

In accepting this notation at the conference, it was decided that in order to preserve historic continuity it should be used in conjunction with the Schoenflies notation for a period of years, as, *e.g.*, $V_h^{16} - Pnma$, $O^9 - Im3m$.

Crystal Physics.

Since the last Report on this subject in 1929 there have been notable advances in nearly all its branches. Here only three will be dealt with, *viz.*, the growth and solution of crystals, liquid crystals, and the relation between optical properties (including the Raman spectra) and structure. This somewhat arbitrary limitation is rendered necessary by the rapid developments which have been taking place, and it has been thought better to deal fairly fully with a few subjects rather than very shortly with them all.

Growth, Volatilisation, Melting, and Solution of Crystals.

Investigations into the growth, volatilisation, melting, and solution of crystals have been pursued for many years, and this Report includes work carried out before 1929. In order to give as clear an idea as possible of this extensive and involved subject it is treated under the following headings: crystallisation in vapours, melts, solids, and solutions. Each of these four divisions is again subdivided into three main parts, *viz.*, the formation of nuclei, crystallisation, and volatilisation or melting or solution.

Crystallisation in Vapours.—Formation of nuclei. The conditions governing this phenomenon are but little known. Nuclei are formed when a sufficient degree of supersaturation is reached, but what that is in any particular case, and what determines it, is unknown.[5]

Crystal growth. The growth of crystals in a vapour is found to be influenced by (*a*) temperature of formation, (*b*) vapour pressure of the gas at the temperature of growth, (*c*) presence of other gases, (*d*) orientation of the crystal with respect to the direction of flow of the vapour, (*e*) preferential directions of growth, (*f*) size of crystals.

(*a*) Temperature of formation. Although in most of the experiments mentioned below no direct measurements of this quantity have been made, its influence on the formation of crystals may to some extent be estimated from the following facts. F. Koref [6] prepared single crystals of tungsten by decomposing the gaseous hexachloride at 110° with a tungsten filament at 1000°. M. Pirani and W. Fehse [7] produced graphite by decomposing substituted and other hydrocarbons with a glowing carbon filament heated to 1500—2000°; A. E. van Arkel and J. H. de Boer [8] prepared pure titanium, zirconium, hafnium, and thorium by heating a tungsten filament to 2000° in the pure vapours of the metallic tetraiodides, and also the carbides and nitrides of these metals by decomposing the chlorides in the presence of small quantities of gaseous carbon and nitrogen compounds respectively. E. Sutter [9] produced crystals of α-, γ-, and δ-iron by decomposing a mixture of ferric chloride vapour and hydrogen by means of a tungsten or iron wire heated to the appropriate temperature. M. Straumanis [10] found that the best crystals were produced when the vapour of zinc or cadmium condensed on a surface a few degrees below the melting point.

(*b*) Vapour pressure of the gas at the temperature of growth. Van Arkel and de Boer [8] used their metallic iodides at atmospheric pressure, but Koref [6] obtained a more coherent deposit, whose

[5] M. Volmer and A. Weber, *Z. physikal. Chem.*, 1926, **119**, 295.
[6] *Z. Elektrochem.*, 1922, **28**, 511. [7] *Ibid.*, 1923, **29**, 168.
[8] *Z. anorg. Chem.*, 1925, **148**, 345. [9] *Diss.*, Greifswald, 1927.
[10] *Z. physikal. Chem.*, 1931, [*B*], **13**, 316.

crystals were single, if the vapour pressure of the tungsten hexachloride–hydrogen mixture was at 12 mm. of mercury. The temperature of the chamber was 110° and the boiling point of the hexachloride is 347°. M. Pirani and W. Fehse [7] also found that low pressures favoured the growth of large crystals, better graphite crystals being obtained at a pressure of 2 mm. of carbon tetrachloride than at pressures up to 25 mm. Straumanis [10] concluded that a high density in the atomic stream favoured the growth of large cadmium and zinc crystals. (Miss) C. F. Elam [11] prepared crystals of α-, β-, and γ-brass from copper by heating it in the vapour of zinc. Which compound of brass was formed depended on the temperature and vapour pressure of the zinc.

(*c*) Presence of other gases. In Koref's experiments, hydrogen seemed to have no influence on the deposition of crystals, but van Arkel and de Boer found that because of chemical action any compound of carbon or nitrogen inhibited metallic deposition entirely. In general, it appears that inert gases hinder the distillation of a volatile solid from one part of the container to another. P. Kapitza [12] found that bismuth formed an amorphous deposit when distilled on a cold surface, but a crystalline one on a hot surface. The same phenomenon was observed long ago when films of bismuth, silver, and gold were spluttered on to glass plates.[13]

(*d*) Orientation of the crystal with respect to the direction of the flow of the vapour. M. Volmer [14] distilled a beam of zinc atoms, allowing them to impinge on an inclined glass plate. He showed that the crystals oriented themselves, the (0001) plane growing with its normal parallel to the beam. This was also observed with cadmium atoms. Straumanis [10] found that the basal plane in zinc and cadmium was usually parallel to the surface of the glass tube on which they were grown. In Koref's experiments the orientation of the tungsten crystal was determined solely by the original orientation of the core. Pirani and Fehse found that the graphite crystals invariably grew with the normal to the basal plane perpendicular to the rod.

(*e*) Preferential directions of growth. M. Volmer and I. Estermann [15] condensed the vapour from mercury at − 10°, in the absence of inert gases, on a surface at − 63°. Small hexagonal plates parallel to (0001) were formed, 10,000 times as wide as they

[11] *J. Inst. Metals*, 1930, **43**, 217.

[12] *Proc. Roy. Soc.*, 1928, [*A*], **115**, 358.

[13] J. Patterson, *Phil. Mag.*, 1902, [vi], **4**, 652; J. A. Becker and L. F. Curtis, *Physical Rev.*, 1920, **15**, 457; F. K. Richtmyer and L. F. Curtis, *ibid.*, p. 465.

[14] *Z. Physik*, 1921, **5**, 31.

[15] *Ibid.*, 1921, **7**, 13.

were thick. When about 0·3 mm. across, they fluttered down. The enormous disparity in the dimensions shows the power of the directive crystalline effect. The theory advanced to explain the unexpectedly rapid rate of growth is that mercury atoms impinging on the plate did not bounce off, but wandered over the surface, increasing the number of atoms which could become attached to the edges of the growing plate. This marked directional effect seems to be exhibited more strongly in crystals grown from vapours than in those from melts and solutions. In the Reporter's (W. A. W.) own experience, sublimed crystals of naphthalene, $CrCl_3$, $FeCl_3$, $AlCl_3$, MoO_3, AsI_3, SbI_3, and BiI_3 all occur in very thin plates, whereas from the melt or solution the tendency is for them to occur in more equally developed forms. Zinc and cadmium also grow in thin hexagonal plates, the step-like surface of which shows that they have grown from the inside outwards. Observations on crystals grown from melts and solutions suggest that their growth starts at the edges and spreads inwards.

(*f*) Size of crystal. Koref observed that after the single crystalline rods, obtained by decomposing tungsten hexachloride vapour, had reached a certain diameter they ceased to grow as single crystals, small ones growing on the sides in random orientations. Size plays so important a rôle in growth from fusion that it seems likely that much remains to be discovered on the effect of size on crystallisation from the vapour.

Volatilisation. G. Aminoff [16] has shown that crystals of thymol, ammonium chloride, α-sulphur, etc., show preferential directions of volatilisation. Spheres were allowed to evaporate and the resulting facets photographed. Straumanis [10] has investigated the details of the process in cadmium by lowering the vapour pressure in the vessel in which cadmium crystals have been growing. Pits developed in the basal plane similar to the etch pits obtained by solution, and showed the same characteristic thickness of step observed on the edges of crystals grown in the vapour.

Crystallisation and Solution in Melts.—Formation of nuclei. Whereas some substances crystallise from a melt very readily, others may be supercooled and remain amorphous for an indefinite period. The origin of the nuclei from which the crystals arise has led to much speculation and experimental work. Some crystalline substances when raised just above their melting points and then cooled recrystallise readily, but if heated to a considerably higher temperature they can become supercooled before crystals reappear. This would suggest that nuclei can persist in an apparently fused substance, a supposition supported by the theoretical work of

[16] *Z. Krist.*, 1925, **61**, 373; 1927, **65**, 23.

R. Bloch, Th. Brings, and W. Kuhn.[17] L. Graf [18] found it necessary to heat copper, silver, and gold about 150° above their melting point in order to get good single crystals, free from small disoriented ones. E. Scheil,[19] A. Goetz,[20] and A. G. Hoyem and E. P. T. Tyndall [21] have found a similar treatment necessary in preparing crystals of aluminium, bismuth, and zinc. After cooling below the melting point, crystallisation may be induced in various ways. A sharp blow with a hammer on an anvil can induce it just below the melting point in water, benzene, and fused hydrated calcium chloride.[22] Scratching the inside of a vessel containing a supercooled liquid with a glass rod is known to promote crystallisation, also exposure to air, or impregnation by dust particles. Hoyem and Tyndall [21] found that in growing single crystals by gradually drawing a rod out of the melt, other crystals arose with a random orientation unless the surfaces were kept free from impurities. Although the Reporter can find no account of it, it seems probable that crystalline particles of isomorphous substances act as nuclei when put into a supercooled melt. H. Pollatschek [23] found that salol crystallised more rapidly in a copper than in a glass tube, under similar conditions of supercooling, so that measurements on the rate of crystallisation could not be made in the former. A common practice at the Geophysical Laboratory, Washington, when dealing with artificial silicates which prove very slow in crystallising, is to take the glass which results on cooling the melt, pound it to a fine powder, heat it, and cool it, and repeat the whole process many times. This apparently accelerates the rate of crystallisation. There is an analogy here with the cold working of metals which must be performed before a polycrystalline material can be made to recrystallise as a single crystal. The pounding of the glass or the shaking of viscous liquids may be methods of setting up strains which predispose them towards crystallisation. W. Kondoguri [23a] has investigated the increase in the number of nuclei formed in a given time due to the application of an electric field to crystallising salol and piperine.

Growth. The factors which influence the growth of crystals from a melt are : (*a*) temperature gradient at the surface of the crystal, (*b*) thermal conductivity of the solid, (*c*) viscosity of the melt—degree of supercooling, (*d*) impurities, including dissolved gases, (*e*) state of strain in solid, or a magnetic field, (*f*) relative size

[17] *Z. physikal. Chem.*, 1931, [*B*], **12**, 415.
[18] *Z. Physik*, 1931, **67**, 400.
[19] *Z. Metallk.*, 1929, **21**, 124.
[20] *Physical Rev.*, 1930, **35**, 193.
[21] *Ibid.*, 1929, **33**, 84.
[22] J. Young and W. van Sicklen, *J. Amer. Chem. Soc.*, 1913, **35**, 1067.
[23] *Z. physikal. Chem.*, 1929, **142**, 289.
[23a] *Z. Physik*, 1928, **47**, 589.

parallel and perpendicular to the direction of growth, (*g*) specific characters of crystal directions.

(*a*) Temperature gradient at the surface of the crystal. F. Stöber[24] has shown that in order to get large flawless crystals of sodium nitrate from a fused melt, it is necessary to adjust the temperature gradient near the surface of the growing crystal very carefully. Ideally, the isothermal surfaces are made parallel to the crystal surface, and the crystallisation front advances at the same speed as the isotherms. To enable this to happen, the temperature gradient is maintained at such a value that the liquid near the crystal is as mobile as possible, since the velocity of crystallisation falls with increasing viscosity [see (*c*), below]. P. Kapitza[12] found in growing bismuth crystals from the melt that a strong temperature gradient was required perpendicular to the (111) plane if the crystals were to be flexible. A theory on the rate of crystallisation in its relation to the thermal constants of the solid and melt, and the temperature gradients, has been given by H. Pollatschek.[25]

(*b*) Thermal conductivity of the solid. In a discussion of the attempts to make artificial diamonds, Stöber points out that Moissan found it necessary to cool the iron containing the carbon very rapidly, whilst other workers using silicate melts had to give cooling periods of the order of weeks. This difference he attributes to the different thermal conductivities of iron and silicates. Both require the temperature gradient at the surface of the growing crystals to be great enough to prevent the melt becoming too viscous. The outside of the iron must therefore be cooled to set up this gradient, whilst it arises only too easily in the silicates.

(*c*) Viscosity of the melt. If the melt becomes too viscous, the crystallisation becomes slow. If the supercooling is large and at the same time rapid, the melt may solidify to a glass. The rate of growth plotted as a function of the temperature in pure glycerol[26] gives a curve starting from zero at the melting point, rising to a maximum about 10° below this temperature, and then falling again to zero. Probably this is typical of many melts.

(*d*) Impurities, including gaseous inclusions. Stöber[27] found that a growing single crystal had the remarkable property of rejecting impurities. Copper and glass spheres dropped on a crystal of sodium nitrate, growing in a crucible from the bottom upwards, were pushed up by the crystal surface as it rose. This also occurred with the minute air and water bubbles which are always present when the commercial product is melted. When the melt was saturated with

[24] *Z. Krist.*, 1924, **61**, 306. [25] *Z. physikal. Chem.*, 1929, **142**, 289.
[26] M. Volmer and M. Marder, *ibid.*, 1931, **154**, 109.
[27] *Chem. Erde*, 1931, **6**, 357.

quartz grains, these could not be ejected and a single crystal grew round them, with a texture closely simulating that of Fontainebleau sandstone. The same power of ejecting impurities is found in benzophenone,[28] when it is contaminated with certain dyes. The crystals grow quite colourless if the crystal is allowed to grow in optimum conditions, but if the degree of supercooling is increased the dye is taken up by the crystal quite regularly, giving rise to pleochroism. The mixture can show "Entmischung," the dye separating out as inclusions, leaving the crystal body clear. It has been suggested that the flexibility of bismuth crystals depends upon the amount of impurity, but Kapitza has shown that single crystal rods of bismuth may be flexible in one half and brittle in the other, the temperature gradient at the growing surface being the determining factor.[12] Graf,[18] on crystallising copper, found that the following impurities were not ejected: 0·4% copper oxide, 0·03% sulphur, 0·02% iron, but that they were uniformly distributed through the crystal. P. W. Bridgman [29] found that gaseous impurities had a bad effect on the growth of metal crystals, but Graf [18] obtained the same crystals of copper, silver, and gold whether he grew them in a vacuum or in an inert gas. Hoyem and Tyndall [21] found on preparing single crystals of zinc (containing 0·000025% As, 0·028% of matter oxidisable by permanganate as Fe, and 0·0020% of chlorides) by withdrawing a rod from the melt, there was a tendency for particular orientations to change gradually, whereas with a purer metal (0·000025% As, 0·0056% of matter oxidisable as before) the change was sudden.

From these examples it is clear that we must distinguish between two types of impurity, those which can accommodate themselves to the lattice, and are taken up in solid solution, and those which cannot be taken up in this way, *e.g.*, oxygen in aluminium. This kind of impurity tends to be pushed out of the crystal as it grows, but if the viscosity of the melt is too high, or the volume of the impurity too great, this becomes impossible, and the impurity becomes embodied in the crystal.

(*e*) State of strain in the solid, and the effect of a magnetic field. Hoyem and Tyndall [21] inoculated molten zinc with a single crystal of known orientation and proceeded to withdraw it as a single crystal rod, keeping the rate of withdrawal and the temperature gradient above the level of the molten zinc constant. They found that the bath of zinc had to be kept within a small range of temperature if the orientation was to remain the same throughout the withdrawal, for beyond the limits of this range the direction of the

[28] G. Tammann and E. Laass, *Z. anorg. Chem.*, 1928, **172**, 65.
[29] *Proc. Amer. Acad.*, 1925, **60**, 305.

hexad axis changed through about 50°, independent of the orientation of the seed crystal. Their conclusion, that "the temperature gradient existing in the liquid zinc just before it solidifies is the main factor determining the continued and successful growth of a particular orientation," seems to be unproven, since they did not investigate other possible influences, such as change in the rate of withdrawal. It appears likely that it may be due to the zinc gliding on the basal plane, the temperature having a secondary effect by controlling the weight of the just solidified portion. The observations are analogous to those made by Kapitza,[12] who found it impossible to grow a crystal of bismuth with its (111) plane perpendicular to its length if it were subjected to the slightest strain while cooling. A. Goetz [30] has investigated the effect of growing a part of a single crystal of bismuth in a magnetic field. The two halves of the crystal show different densities and specific resistances.

(*f*) Relative size parallel to the direction of growth and perpendicular to it. F. Stöber [31] brings forward much evidence to show that the rate of growth in a particular direction is inversely proportional to the area of a perpendicular cross-section. A quantitative test of this assumption was made on crystallising sodium nitrate. By slow cooling, the whole content of a nickel crucible could be made to grow as a single crystal, with its optic axis perpendicular to the isotherms. More rapid cooling caused the growth of a number of parallel rods, having the same orientation as the single crystal. The average area of the rods varied approximately as the inverse of the time taken over cooling. Stöber applied this relation to some hitherto unexplained results obtained by other workers.[32] Another application of this principle is to be found in the rapid rates of growth often seen in crystals which form needles, thin plates, and sheaf-like growths. In attempting to explain the relation between rate of growth and area of growing face, Stöber seems to be on less certain ground. He assumes that the gravitational attraction which one atom exerts on an approaching atom is primarily responsible. The gravitational field near to a single row of atoms must be periodic and may possess marked directive properties. These are very much less at the surface of an actual crystal because the atoms in the body of the crystal smooth out the variations in the forces produced by the single row of atoms. Similarly, the greater the area of a face the less is the force of attraction experienced by an atom approaching the face. On this ground

[30] *Physical Rev.*, 1930, **34**, 193; **35**, 193; **36**, 1752.
[31] *Chem. Erde*, 1931, **6**, 453; *Jahrb. Min.*, Beil.-Bd., [*A*], 1928, **57**, 156.
[32] M. Volmer and G. Adhikari, *Z. Physik*, 1925, **35**, 170; F. Bernauer, *Jahrb. Min.*, Beil.-Bd., [*A*], 1928, **57**, 1131.

Stöber attempted to explain why slowly cooled sodium nitrate grows as a single crystal whilst the rapidly cooled melt forms narrow crystal rods. This explanation can scarcely be correct because of the enormous disparity between the crystal and atomic dimensions. It can hardly make any difference to the gravitational forces at the face of a growing crystal whether it is a millimetre or a centimetre across. But if every new layer of a growing crystal had to start at a corner or edge and then travelled inwards, a crystallisation front would be able to advance more rapidly if the number of edges and corners were increased by the decrease in the area of the individual crystals. (Sir) H. Miers[33] suggests that the crystal itself and the particles about to be deposited are in mechanical resonance. Were this so, then the characteristic frequency of a large crystal would be low and might correspond to a slow rate of deposition, thus accounting for Stöber's empirical result.

(*g*) Specific characters of crystal directions. All substances which crystallise as needles or plates do so with a definite relation to the crystal axes. Stöber[34] suggests that the crystallisation front of sodium nitrate is always perpendicular to the optic axis because it is the direction of greatest heat conductivity. It would be valuable to establish this relation for other crystals. Whilst this type of explanation gives an indication of the direction of elongation, the reason why some crystal faces appear rather than others remains obscure, and, at present, we cannot do more than attribute to each face a specific rate of growth.

(*h*) The process of melting. The study of the behaviour of crystal faces during melting is made very difficult by the immediate solidification of some of the adhering liquid on removing it from the melt. The *X*-ray method used by A. Müller[35] is very powerful. A fine beam of *X*-rays was directed on some molten paraffin very near the surface of a crystal of the same substance. For a small range of temperature above the melting point, the diffraction pattern showed that there was still a considerable amount of orientation among the molecules. Apparently the crystal dissolves in sheets of molecules. A similar orientation of the molecules of a liquid near to a solid surface is well brought out in the experiments by J. J. Trillat.[36]

Growth of Crystals in the Solid State.—An immense literature has grown up during the last few years on the recrystallisation of solids, but it is principally concerned with problems of strain and mechanical

[33] *Science Progress*, 1907. [34] *Chem. Erde*, 1931, **6**, 440.

[35] *Proc. Roy. Soc.*, 1930, [*A*], **127**, 417.

[36] See summary, "Fortschritte der Röntgen Forschung," p. 33; Akad. Verlag. Ges., Leipzig, 1931.

properties in metals. This Report does not include this work except as illustrating particular features of solid recrystallisation which are dealt with here. References to a few papers dealing with the recrystallisation of metals are given.[37]

Formation of nuclei. Nuclei for recrystallisation do not arise unless the material has been strained to some extent; generally only a small deformation is required. In some cases they may be latent, as they may not develop for hours after other nuclei have grown into grains of considerable size. The rate of formation of nuclei for a given degree of deformation is higher the higher the temperature. The presence of impurities generally facilitates nucleus formation.

Growth. The conditions which appear to affect the growth of an already formed nucleus are: (*a*) temperature, (*b*) impurities, (*c*) orientation of neighbouring grains.

The size of the crystal seems to have no effect on the growth, contrary to what one might expect, since it influences growth from melts and vapours.[38]

(*a*) Temperature. Tammann and Dreyer [38] have investigated the effects of cold working and subsequent heating on camphor, pinene hydrochloride, and ice. The substances were compressed to about a quarter of their original thickness and then annealed at various temperatures. The more powerful the compression and the nearer the annealing temperature lay to the melting point the greater was the rate of advance of the crystal grain boundaries. The same general result has been found to hold good in metals. Apparently the rate of recrystallisation tends to infinity as the temperature approaches the melting point. The limit is set by the impurities which the crystal has to push out of the way.

(*b*) Impurities. Most work on the recrystallisation of metals shows that large single crystals can only be grown in pure substances. A considerable quantity of impurity not only causes spontaneous growth from many centres but appears to hinder the growth of the grains by forming a kind of skin round the boundary of the growing crystal. The existence of these skins was demonstrated by Tammann and Dreyer: distillation of the substances from the plate after the recrystallisation left a fine residue outlining the boundaries of the crystal grains, the rest of the plate being quite clean. The skin formed round metal grains may be similarly demonstrated by dissolving away the metal without evolution of gas. This expulsion

[37] G. Tammann, *Z. anorg. Chem.*, 1930, **185**, 1; A. E. van Arkel and J. J. A. Ploos van Amstel, *Z. Physik*, 1930, **62**, 43, 46; W. G. Burgers, *ibid.*, 1930, **59**, 651; U. Dehlinger, *Ann. Physik*, 1929, [v], **2**, 749.

[38] R. Karnop and G. Sachs, *Z. Physik*, 1930, **60**, 464; G. Tammann and K. L. Dreyer, *Z. anorg. Chem.*, 1929, **182**, 289.

of impurities is not surprising since the same phenomenon is found in the growth of crystals from melts. This may give the key to the spontaneous growth of crystals after deformation, which, causing the grains to slip along certain planes, breaks the skins of impurities, and allows the pure material of one grain to come into contact with that of another.[37] A less deformed crystal can then proceed to grow at the expense of a more deformed one. This expulsion of impurities may also be able to account for Schiller structures, observed in various minerals. Under the microscope they are seen to consist of orientated, regularly-shaped inclusions, bounded by crystal faces. They are usually attributed to a change in composition on cooling (" Entmischung "), the components which separate out taking up their position in cracks previously dissolved out by magmatic solutions. In the light of the facts given above, it appears more probable that the original crystal suffered a strain and, in consequence, broke up into a much finer grained material. Subsequent cooling caused " Entmischung " to occur, and the rejected components were thrown out as insoluble material. During recrystallisation that followed the straining (which would be facilitated by a rise in temperature, but could take place slowly without it), the impurities would migrate to the boundaries of the grains and there crystallise out. The regularity of the inclusions is to be explained by the known regularity of the glide planes produced by pressure. The homogeneity of the matrix is due to the recrystallisation after the ejection of the impurities. A similar explanation may also apply to the calcium-rich minerals such as epidote zonally arranged in recrystallised albite. Deformation may also be produced by γ-radiation,[39] and recrystallisation in sodium chloride then occurs at room temperatures. Przibram has taken cinematograph photographs of large grains being produced during the recrystallisation.

(*c*) Orientation of neighbouring grains. Tammann and Dreyer notice a very marked tendency in crystals of camphor and ice for the basal plane, if suitably oriented, to grow at the expense of all other planes. The great advantage of experimenting with transparent doubly refracting crystals is apparent here, a similar investigation in metals being far more difficult to carry out.

Growth from and Solution in Solvents.—Formation of nuclei. When the supersaturated aqueous solution of an inorganic salt (*e.g.*, sodium nitrate) is cooled, a temperature is reached at which it is possible by inoculation to cause crystallisation. At the same concentration, crystallisation may also be induced by other methods, such as violent shaking, scratching the side of the vessel with a glass rod, violent

[39] K. Przibram, *Z. Elektrochem.*, 1931, **37**, 535.

impact, etc. Although other workers have contradicted his assertion, it seems probable from the work of Miers [40] that there is a maximum temperature (about 10° below the first temperature at which it is possible to cause crystallisation by inoculation) at which the solution if left quite alone will crystallise spontaneously. The long controversy which has continued over the existence of the "supersaturation temperature" for a given concentration cannot be more than mentioned here. If the saturated solution be inoculated with an isomorphous substance, crystals can be caused to deposit on this as nucleus, but the degree of supersaturation required is dependent on the kind of nucleus used.[41] The same phenomenon has been shown by M. Volmer and A. Weber,[42] who investigated the degree of supersaturation required to cause crystals of one inorganic salt to grow on various insoluble substances. They mention that sodium nitrate tends to grow on the edges of calcite and that the side faces of barytes, gypsum, and mica cleavage plates were active in precipitating this salt. In some cases the deposition of foreign nuclei is clearly subjected to a directive force, *e.g.*, potassium iodide on muscovite, cyanite on staurolite, potassium chloride on rock-salt.

Growth. The conditions governing the growth of a crystal from solution are: (*a*) temperature, as it affects the degree of supersaturation, (*b*) impurities in the solution, (*c*) size and shape of the crystal, and effect of surrounding faces, (*d*) specific characters of certain crystalline directions.

(*a*) Temperature as it affects the degree of supersaturation. Following the general reasoning applied to many physicochemical problems, the rate of increase of the distance x between two parallel faces on a crystal has been shown [43] to be given approximately by the formula $dx/dt = k(c - c_0)$, where c is the prevailing concentration at time t, and c_0 is that corresponding to equilibrium between salt and solution. The habit of the crystals has been observed to change with the degree of supersaturation.[44] In addition to changing the degree of supersaturation, temperature must also change the viscosity, but the effect of this on the rate of growth does not appear to have been investigated.

(*b*) Impurities in the solution. The influence on the crystal habit of impurities dissolved in the solution has been known in certain cases for a very long time. The work of H. E. Buckley [45] has

[40] Inst. Metals, May Lecture, 1927.
[41] I. N. Stranski and K. Kuleliew, *Z. physikal. Chem.*, 1929, **142**, 467.
[42] *Ibid.*, 1926, **199**, 277.
[43] M. le Blanc and W. Schmandt, *ibid.*, 1911, **77**, 614.
[44] A. Shubnikov, *Z. Krist.*, 1914, **53**, 433.
[45] *Ibid.*, 1930, **73**, **443**; **75**, 15; **76**, 147; 1931, **78**, 412; **80**, 238.

shown how extensive and remarkable these effects are with a large number of inorganic salts. He has also attempted a correlation of the lattice dimensions on the crystal faces whose growth rates are most affected by the impurity and the atomic distances characteristic of the dissolved ionic impurity. Progress in this subject is not easy, and there are few cases where such a correspondence exists. I. Kurbatov [46] has shown how the occurrence of large crystals, particularly of sparingly soluble substances, *e.g.*, barytes, may be explained by the occurrence of supersaturated solutions of barium and sulphate ions in non-equivalent proportion. This state is established by soluble impurities. Frl. Buschendorf [47] has described an occurrence of fairly large crystals of barytes which must have grown during historical times, and an analysis of the solution in which the crystals occurred showed that it contained barium, calcium, iron, carbonate, and sulphate ions.

The mechanism by which a change in habit is brought about by dissolved impurities is still obscure. The theoretical work of W. Kossel [48, 49] and I. N. Stranski [50] indicates that, as in the case of crystallisation from melts, each new layer has to start at a corner or edge and then spreads across the face at a great speed. The time taken in crystallisation thus depends on the probability of a new set of atoms being oriented at a corner or edge. If an impurity be introduced, and this adheres to the growing surface, it is clear that the rate of spreading of the layers across the surface will be impeded by the presence of the foreign ions. This process is well illustrated by the case of rock-salt and urea. The occurrence of the octahedral face in the former means that this is slower growing than the cube. Since the octahedral face in rock-salt contains only negative or positive ions, it is to be expected that a polar body like urea will be more likely to become attached to this face than to the cube face with its mixed ions. This would cause the (111) faces to have a rate of growth slower than normal, and to be predominant in a crystal grown in such a solution. The absorption of dyes on the surfaces of growing crystals [51] shows that the impurity is very closely associated with the surface during growth.

(*c*) Size and shape of the crystal, and the effect of surrounding faces. M. Bentivoglio [52] has shown that the rate of growth of several crystals, including the double sulphates of the general formula $R'_2R''(SO_4)_2,6H_2O$, is, over a range of 0·3—6·0 mm., inde-

[46] A. Shubnikov, *Z. Krist.*, 1931, **77**, 164; *A.*, 677.
[47] *Centr. Min.*, 1930, 467. [48] *Nach. Ges. Wiss. Göttingen*, 1927, 135.
[49] *Naturwiss.*, 1930, **18**, 901. [50] *Z. physikal. Chem.*, 1928, **136**, 259.
[51] T. S. Eckert and W. G. France, *J. Amer. Ceram. Soc.*, 1927, **10**, 579; F. G. Keenen and W. G. France, *ibid.*, p. 821.
[52] *Proc. Roy. Soc.*, 1927, [*A*], **115**, 67.

pendent of their size. Certain inorganic salts, such as the alums, Rochelle salt, potassium ferrocyanide, etc., can be grown to very large crystals, and it seems that there could not be much reduction in the rate of growth for a given amount of supersaturation, for if so they could not grow to this extent with such rapidity. The shape of the crystal is determined by the fact that it tends to be bounded by the slowest-growing faces, and the rate at which these develop is, according to Bentivoglio, not affected by other faces which may be present except when the latter develop so rapidly that they impoverish the solution surrounding the more slowly-growing faces. K. Spangenberg [53] and A. Neuhaus [54] have shown that for various alums and for rock-salt the rate of growth for a given form depends on what other forms are present. If other faster-growing forms are present, the form grows more slowly than when the other forms grow more slowly. In spite of the careful measurements of the above authors, one is compelled to remember that under other conditions where the supersaturation is greater the rate of growth of faces of the same form is not the same for all faces of that form. For instance, potassium chloride crystallising from a supersaturated solution on a microscope slide almost invariably shows some crystals which have grown into long needles, bounded by the cube faces only. Potassium permanganate crystallising slowly grows equably, but from a drop on a microscope slide it often crystallises in a mass of fine needles. It is very difficult to understand how a cubic crystal can have a different rate of growth for two faces of the cubic form, under identical conditions.* One of the most important observations that remain to be made is the variation of the concentration gradients over different faces of a cubic form when they are growing at different rates.

(*d*) Specific characters of certain crystalline directions. An explanation of the action of urea on the habit of rock-salt has been attempted in terms of the different solubilities of the cubic and the octahedral faces. Such an explanation was dismissed by the experiment of F. G. Cottrell,[56] who showed that an octahedron of

[53] *Jahrb. Min.*, Beil.-Bd., [*A*], 1928, **57**, 1197.

[54] *Z. Krist.*, 1928, 15.

[55] *Min. Mag.*, 1908, **15**, 39.

[56] *J. Physical Chem.*, 1906, **10**, 52.

* (Sir) H. Miers [55] suggests that the needle-shaped crystal is due to the solution's being in the labile state, *i.e.*, at a concentration such that it can produce nuclei spontaneously. He considers that the needle advances continuously into a labile region of the solution, and that the sides which do not grow are surrounded by a layer of metastable liquid. It is difficult to understand how this can be the explanation, because these same quiescent sides start to grow in this supposedly metastable region as soon as the end of the needle ceases to grow rapidly.

rock-salt grown from a urea-bearing solution remained unaffected when immersed in a pure solution of salt saturated at the same temperature. Stranski and Kuleliew,[41] in investigating the deposition of sodium nitrate on the isomorphous substances calcite, siderite, and rhodocrosite, found that the nitrate crystals deposited first at the corners and then at the edges. Deposition in the middle of the rhombohedral faces occurred last of all, and then only in cracks or irregularities. Hopper crystals may be grown from supersaturated solutions of sodium chloride and from several of the isomorphous substances. Here the growth is confined entirely to the edge, and seems to support the supposition that in a normal crystal deposition always starts at the corner or edge, the layer continuing right across the face.* There may therefore be two factors determining the differences in the rate of growth perpendicular to the various faces: (i) the probability of the layer beginning at the edge or corner of a face, and (ii) the rate at which the layer can complete itself.

Solution. A crystal bounded by plane faces in general has its faces rounded by dissolution, and other crystal forms are developed on it. A rock-salt cube dissolving in an aqueous solution of urea first develops faces approximately of (25, 1, 0) and then the icositetrahedron (25, 1, 1) which is unchanged in shape on further solution.[57] Etch pits and figures of various kinds are the usual phenomena accompanying the first stage of solution. A great deal of work has been done on the "geometrical" aspect of solution. Spheres of various substances have been dissolved in various agents, and the final shape taken up by the body (which does not alter on further action of the agent) has been examined.[58]

The factors which affect solution phenomena are: (*a*) temperature, as it affects the degree of under-saturation, (*b*) impurities in the solution, (*c*) specific characters of certain crystal directions.

(*a*) Temperature as it affects the degree of under-saturation. The rate of solution, measured in mg. per unit area, has been found to be approximately proportional to the degree of under-saturation (difference between momentary concentration at the crystal face and the saturation value).[43] There seems to be but little difference between growth and solution velocities for the same degree of under- and super-saturation. With a small degree of under-saturation, the final end-shapes are bounded by relatively sharp edges, whereas with a large under-saturation it is usually much more irregular.[57]

[57] W. Schnorr, *Z. Krist.*, 1915, **54**, 309.

[58] For summary of this work, see *Jahrb. Min.*, Beil.-Bd., 1929, **60**, 111.

* For theoretical confirmation of this see Refs. (48), (49), and (50).

(*b*) Impurities in the solution. Remarkable changes in the habit are brought about by solution in the presence of impurity. Recent work of G. Friedel [59] and L. Royer [60] is still more surprising. They found that calcite gives etch-figures symmetrical about (011) in an inactive, but unsymmetrical in an active, solvent. Dolomite gives etch-figures on (100) and ($\bar{1}$00) enantiomorphous with respect to (01$\bar{1}$) in an inactive solvent, but, in an active, quite dissimilar figures. Calamine etched by an inactive solvent gives pits symmetrical with respect to a plane parallel to (100), but an active solvent indicates that a diad axis parallel to *c* is the only symmetry present. Further, if a *d*-acid is etched by a *l*-alcohol, the etch figures are enantiomorphous with those of a *l*-acid etched by a *d*-alcohol. They are quite different from those obtained by etching a *d*-acid with a *d*-alcohol. So far, these results have not been substantiated by other workers, and in one case [61] contradictory evidence was obtained. Etch figures are of so much importance in crystal structure work that it is desirable that this phenomenon should be placed on a sure footing.

(*c*) Specific characters of certain crystal directions. An enormous amount of data has been collected about this subject, and by working with single crystals of metal methods have been devised to eliminate the effect of shape, impurities, and strain in the crystal. The solution figures and " end-shapes " which have been obtained are very elegant, but quite inexplicable in terms both of structure and of the character and behaviour of the molecules in solution.

Conclusion. The difference between crystal growth in a vapour and in a liquid, be it a melt or solution, is that the molecules or atoms in a vapour are usually unco-ordinated as they come near a crystal, whereas the immediate liquid environment of a crystal is almost certainly a well-ordered one. A problem still to be investigated is that of the " pre-crystal " existing in the liquid, and the factors which influence it. In the researches outlined above, no attempt has been made to explain why crystals have the directive forces which play such an important part in their growth. It is, however, clear that in a general kind of way, there are certain types of habit which are associated with a corresponding structure; but it is almost impossible to draw any certain conclusions from the mass of information that has been collected on the growth and solution of crystals, because very few of the aspects have been investigated from all sides, and insufficient systematic work has been carried out.

[59] *Compt. rend.*, 1927, **184**, 789.

[60] *Bull. Soc. franç. Min.*, 1930, **53**, 350; *Compt. rend.*, 1929, **188**, 1176, 1303; **189**, 932; 1930, **190**, 503.

[61] T. M. Lowry and M. A. Vernon, *Z. Krist.*, 1929, **70**, 384.

Liquid Crystals.

Half a volume of the *Zeitschrift für Kristallographie* (1931, **79**, Hefte 1/4) has been devoted to the problem of liquid crystals. It was the editor's aim to promote the study of the subject by enabling the workers to arrive at an accepted terminology, and to settle controversies by discussion. The first part of the volume contains contributions by the investigators who are interested in the subject, largely original, but also containing useful reports on other people's work. This is followed by criticisms of one another's work, which give a useful summary of current views. In a publication which is presumably representative of European work, it is regrettable that there is not a single English contribution. Short summaries of the papers are given below.

The physical properties of the mesomorphous stases in general, and their importance as a principle of classification (G. Friedel and E. Friedel). The word " stasis " is defined as applying to the different structural types of matter, *e.g.*, the crystalline stasis, or gaseous stasis, thus setting free the usual words " state " or " form " for their more ordinary meanings. " Mesomorphous " is coined to describe the liquid-crystalline stases. To avoid confusion in dealing with those mesomorphous stases which may show a variety of appearances under the microscope, the word " structure " is reserved for a particular molecular state, and the word " texture " for homogeneous states in which the structure is constant. Thus, the texture may vary while the structure stays constant. There are four stases in which a substance may occur, but not more than four : the solid crystalline, the smectic, the nematic, and the amorphous liquid. Mesomorphous stases differ from crystalline ones in having fewer vectorial properties. They are spontaneously anisotropic, and change reversibly from one stasis to another at a definite temperature which is determined by the pressure. The smectic stasis is characterised by being very viscous, whereas the nematic is mobile. The authors have studied in great detail the optical character of many of the substances showing these properties. Both smectic and nematic stases are uniaxial, and under certain conditions they show interference figures in convergent polarised light. Certain cholesterol derivatives are nematic and show enormous rotatory power. The differences in the X-ray pattern shown by smectic and nematic stases are also dealt with.

Chemistry of liquid crystals (D. Vorländer). All substances which on melting pass into liquid crystals have long-shaped or flat molecules. There is no distinction, as far as the capacity for forming liquid crystals is concerned, between those molecules

which are symmetrical in their chemical formula and those which are not. Polymorphism is very well marked in some liquid crystals, *e.g.*, in *p'*-phenylbenzal-*p*-aminocinnamic acid ethyl ester there are five melting points and four liquid-crystalline states. These are clearly differentiated by their viscosity, optical properties, and latent heats. Non-pleochroic liquid crystals when arranged parallel show a uniaxial optically positive character, whereas circularly pleochroic liquids are negative in such circumstances. A comparison of the optical properties of a number of organic substances is also given.

Experimental and theoretical basis of the swarm hypothesis in liquid crystals (L. S. Ornstein). The "swarm hypothesis" postulates that a molecule, by its shape or other characters, is able to orientate the molecules around it. The author endeavours on this basis to explain the optical, magnetic, and electrical effects, and the effect of the walls of the containing vessel. The scattering of light by liquid crystals is treated theoretically, and the predictions are verified by experimental observation. A magnetic field produces very marked and rather complicated effects on the opacity of liquid crystals, and changes in the dielectric constant are also well marked. A magnetic field perpendicular to the walls produces a decrease in the dielectric constant by an amount which diminishes as the temperature of the transition to the amorphous liquid is neared. Parallel to the walls, however, it produces a very much smaller increase in the dielectric constant. The explanation given is that the molecules are oriented parallel to the walls of the vessel, and by reason of their mutual action this orientation extends some distance into the liquid. The long molecules are assumed to be anisotropic both magnetically and electrically. They tend to set parallel to the magnetic field, and at right angles to the electric field. Thus the magnetic field perpendicular to the walls of the vessel causes the molecules to turn round and thus to lessen the dielectric constant. When parallel to the walls, however, the magnetic field serves to bring the molecules in the middle of the tube more nearly parallel to the ones near the walls, and so to increase the dielectric constant. The size of the largest molecular group in the liquid crystal comes out to be 3×10^{-6} cm. on the theory set out here. The action of the walls is brought out clearly in the following experiment. A silver plate attached to a thermo-couple is immersed in a liquid crystal. A magnetic field applied perpendicular to the plane of the plate produces a heating effect when switched on, and a cooling effect when switched off. If it is applied parallel to the plane of the plate, no such effect is obtained. The fundamental basis of the swarm hypothesis is given according to classical thermodynamics.

The optics of mesophases (H. Zocher). A discussion is given in general terms of the various optical phenomena of liquid crystals. Explanations of the colours observed are given on the basis of the known structures of mesophases.

X-Ray investigation of liquid crystals (K. Herrmann and A. H. Krummacher). The authors criticise certain conclusions of de Broglie and E. Friedel on the size of the liquid-crystal molecule. The molecule diffracts the *X*-rays into a diffuse ring, which breaks up in a magnetic field into two " brushes," which stretch from the centre outwards, and are orientated so that the line joining them is perpendicular to the direction of the magnetic field. The photograph of phenetoleazoxybenzoic acid allyl ester, obtained with the viscous and mobile phases orientated by the magnetic field, are very similar, the former being the better orientated. Photographs of crystals which had solidified when under the action of a magnetic field show the same orientation though not quite so marked. Measurements of the brushes give mean values for the dimensions of the molecule perpendicular to its length which are in agreement with what we should expect from its known chemical formula and the sizes of atoms.

Dielectric constant (W. Kast). The author is concerned only with mobile liquid crystals, which from their dielectric characters fall into two groups, *viz.*, symmetrical and unsymmetrical molecules. As an example of these, we have anisaldazine,

$$CH_3O{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OCH_3,$$

and *p*-ethoxybenzalamino-α-methylcinnamic acid ethyl ester, $C_2H_5O{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CH{:}CMe{\cdot}CO_2Et$. The substances having symmetrical molecules show a reduction in dielectric constant when the field is perpendicular to the plates of the condenser, and a small increase when parallel. The amount of these changes depends on the temperature, magnetic field, and electric field between the condenser plates. When the unsymmetrical molecules are acted on by a magnetic field parallel to the electric field, there is a small increase in the dielectric constant. These differences are attributed to the tendencies of the symmetrical and unsymmetrical molecules to set themselves respectively parallel to and perpendicular to the condenser plates. By making certain assumptions, the dipole moment of the molecules may be calculated from the experimental data ($\mu = 2{\cdot}3 \times 10^{-18}$). By assuming dipoles to be present, the same theoretical treatment may be used as for paramagnetism. This has been done by Born, who finds a value for μ 50% higher than that observed. The changes of the dielectric constant with constant magnetic field and different electric fields are found. By applying the Langevin formula to the experimental curves, a molecular moment

10^6 times that actually observed is obtained. The conclusion is that groups of dipoles must be present in the anisotropic melt.

Magnetic susceptibility (W. Kast). Both with *p*-azoxyanisole (mobile) and *p*-azoxybenzoic acid (viscous) there is a decrease in diamagnetic susceptibility on passing from amorphous liquid to liquid crystal. The general conclusion from the change of conductivity, of dielectric constant, and of susceptibility with temperature is that the number of swarms decreases with the temperature. The number of molecules which go to make up one swarm is estimated at about 10^5.

Problems of the theory of anisotropic liquids (C. W. Oseen). This contains a mathematical development of a simplified case to show the dependence of the properties of liquid crystals on the temperature.

Of the symmetry groups of amorphous and mesomorphous phases (C. Hermann). MM. Friedel have postulated that (1) the nematic stasis has the centre of gravity of the molecule orientated at random, but that the molecules have their axes more or less parallel; (2) in the cholesteric stasis the directions of the molecular axes form a spiral; (3) in the smectic stasis the centres of gravity lie in parallel planes in addition to all the axes being parallel. E. Alexander and K. Herrmann have assumed that (1) in the nematic stasis the molecules form straight lines, (2) in the smectic and cholesteric stases the molecular centres of gravity form plane nets. C. Hermann proceeds to determine the total number of possible arrangements of the molecular axes, centre of gravity, etc., after making some assumptions about the equivalence of the molecules and the finite size of the constituent atoms. This purely geometrical analysis is quite exhaustive, and the author of it has shown exactly what characteristics the *X*-ray pattern of the various geometrical arrangements should have. The three or four types mentioned above are shown to be particular cases of the twenty possibilities.

On mesomorphous and colloidal systems (W. Ostwald). This is a general account of the nature and properties of all kinds of mesomorphous states. All forms of molecular aggregation—particularly bundles and plates of molecules—are considered, and a series of objections is raised to the swarm theory. A full discussion of the phenomenon of cloudiness and the ultramicroscopic and viscous properties of liquid crystals is given, also the relationship of mesomorphous and colloidal systems.

On the double refraction of thin layers of anisotropic liquids in a magnetic field, and the orientating force within this layer (V. Fréedericksz and V. Zolina). When a liquid crystal is held between a convex lens and a plane glass plate, with a magnetic field perpendicular to the glass plate, and observed in polarised light, a

complicated phenomenon is seen. Up to a certain distance from the centre the field is dark, but beyond this there is a family of very fine concentric bright and dark fringes. The critical boundary between the inner and the outer field is independent of the cleanness of the glass walls; the critical thickness z and the magnetic field H are related by the equation zH = constant = k, where k depends on the temperature. The theory given by Ornstein is able to explain these phenomena. From this theory it may be deduced that the molecules lying on the glass itself do not move at all when the magnetic field is applied. Further, the authors find no evidence of an inner dipole field and do not regard the swarm theory as being essential for the explanation of their results.

The discussion which follows is full of interest, but an account of it cannot be given here. Though many controversial points are argued, there does not appear to be any marked agreement between the various schools of thought.

Optical Properties and Crystal Structure.

Raman spectra of a great many crystals have been determined since the last Report on this subject in 1929. A summary and full bibliography of the work up to 1930 have been given by S. Bhagavantam.[62] The principal groups of crystals which have been examined are diamond,[63] sulphur,[64] inorganic chlorides,[65] calcite and aragonite,[66] inorganic sulphates,[67, 68, 69] carbonates,[68] nitrates,[69, 70] chlorates, bromates, selenates, phosphates,[71] hydroxides, cyanides, and thiocyanates.[72] Certain groups of atoms are found to have characteristic frequencies, and in this connexion the Raman spectra are extremely useful in supplementing the X-ray analysis. Sulphur is a good example of a case in which the existence of polymerisation may be detected by this method. The strong Raman line at 1332 cm.$^{-1}$ in diamond corresponds to a frequency in good agreement with that calculated from its known specific heat properties. The examination of the chlorides leads to the conclusion

62 *Indian J. Physics*, 1930, **5**, 237; *A.*, 1930, 1498.

63 C. Ramaswamy, *ibid.*, p. 97; S. Bhagavantam, *ibid.*, pp. 169, 573; *A.*, 1930, 1345; 1931, 145.

64 P. Krishnamurti, *ibid.*, p. 105; 1931, **6**, 7; *A.*, 997.

65 *Idem, ibid.*, 1930, **5**, 113; *A.*, 1930, 1344.

66 S. Bhagavantam, *Z. Krist.*, 1931, **77**, 43; *A.*, 668.

67 P. Krishnamurti, *Indian J. Physics*, 1930, **5**, 183; *A.*, 1930, 1344.

68 N. Embirikos, *Z. Physik*, 1930, **65**, 266; *A.*, 1930, 1499.

69 C. Ramaswamy, *Indian J. Physics*, 1930, **5**, 193; *A.*, 1930, 1344.

70 P. Krishnamurti, *ibid.*, 1930, **5**, 1.

71 C. Schaefer, F. Matossi, and H. Aderhold, *Z. Physik*, 1930, **65**, 289; *A.*, 1930, 1499.

72 P. Krishnamurti, *Indian J. Physics*, 1930, **5**, 633, 651; *A.*, 146.

that covalent linkings in $HgCl_2$, Hg_2Cl_2, $ZnCl_2$, CdI_2, $SbCl_3$, $BiCl_3$, and PCl_5 are necessary for the Raman effect to occur; compounds possessing only electrovalent linkings do not show Raman spectra, *i.e.*, the chlorides of Li, NH_4, Mg, Ba, Cu(ic), Ag, Cd, Sn(ous), and Th, and the iodides of K and Pb. The Raman spectra of the sulphates show that the sulphate ion is easily deformable, being affected by the degree of hydration, size of the surrounding ions, and the paramagnetism of the kation. The Raman line of the sulphate ion is displaced much less from the exciting line in solution than in the solid except in the case of $MgSO_4,7H_2O$, where the converse is true at certain concentrations of the solutions. In the nitrates, the inactive frequency of the nitrate group appears as a sharp line, and on solution the greatest changes in its frequency are observed in nitrates of the light and the heavy atoms. The results may be summarised by saying that the smaller the volume of the kation the greater the frequency shift from its value in solution. The result of the researches on the XY_3 group confirms the conclusion drawn from infra-red analysis, *viz.*, that all the radicals form three-cornered molecules with four inner frequencies, one of which is inactive. In the XY_4 groups, four frequencies only two of which are active are found, again in confirmation of the work in the infra-red. Sodium hydroxide shows a frequency shift (3630 $cm.^{-1}$) considerably different from that of water (3450 $cm.^{-1}$), and is important in showing how the Raman lines may be used to distinguish between water of crystallisation and of constitution. For the study of crystal structure it seemed that the polarisation of Raman lines would prove most helpful, but up to the present the phenomenon is surrounded with difficulties both experimental and theoretical.[73] Large crystals appear to be necessary and different observers obtain different results. That the Raman lines corresponding to the water in gypsum vary markedly on changing the orientation of the crystal with respect to the incident light and its plane of polarisation, suggests that this phenomenon may be very important as an aid to structure analysis. The temperature variation of the Raman spectrum of quartz and benzene has been studied by (Mlle.) M. J. Ney.[74] She finds that the Raman lines of benzene become broader as the temperature rises, whilst those of quartz do not. This broadening is attributed to molecules which rotate at the higher temperature. This would be an elegant method of showing in any particular case when rotating molecules were present.

[73] C. Schaefer, F. Matossi, and H. Aderhold, *Physikal. Z.*, 1930, **31**, 801; *A.*, 1930, 1344; *Z. Physik*, 1930, **65**, 319; J. Cabannes and (Mlle.) D. Osborne, *Compt. rend.*, 1931, **193**, 156.

[74] *Bull. Acad. Polonaise*, 1931, [*A*], 106; *A.*, 1211; *Z. Physik*, 1931, **68**, 554; *A.*, 668.

The relation between double refraction and crystal structure has been treated by the Reporter [75] in an empirical way. Structures may be divided into the following types, which are characterised by certain degrees of double refraction: (1) layer lattices—strong negative double refraction except when the substance contains hydroxyl ions; (2) chain lattices—strong positive double refraction when the chain is parallel to the optic axis; (3) structures with strongly asymmetric groups—double refraction large, the electric vector of the ray having the higher index being parallel to the shortest bonds; (4) lattices with only symmetrical groups—low double refraction; (5) lattices consisting of a three-dimensional network—low double refraction; (6) certain iron- and titanium-bearing substances—high double refraction which is not due to marked asymmetry in the crystal lattice.

Structures of organic compounds are generally too complicated to permit of any similar generalisations, but in simple cases of long-chain or ring compounds this is not so. Thus, K. Banerjee [76] saw the probable orientation of the naphthalene and the anthracene molecule in their respective crystals from the optical and magnetic properties, and verified his expectations by means of *X*-ray analysis.

CRYSTAL CHEMISTRY.

V. M. Goldschmidt [77] has recently given another illuminating account of the present state of the subject. The multiplication of *X*-ray crystal analyses, with their greater accuracy and trustworthiness, and the development of quantum mechanical theory have brought further confirmation of the essential rightness and fruitfulness of his original assumptions on ionic size and co-ordination. On the theoretical side, the most important work has been the explanation of the physical nature of the effective forces holding crystals together. The fundamental ideas of ionic (electrostatic) cohesion and electron-sharing (valency) bonds have been considered in far greater detail and the relations between them and the less well-known (the molecular and metallic) forces are beginning to appear.

The Homopolar Bond.—For the homopolar bond the most important recent work from the point of view of crystal chemistry is that of J. C. Slater and L. Pauling. The former [78] has calculated inter-molecular distances in molecules and crystals on the assumption that for electron exchange bonds both atoms will be at such a

[75] W. A. Wooster, *Z. Krist.*, 1931, **80**, 495.
[76] *Ind. J. Sci.*, 1929, **4**, 557.
[77] *Fortschr. Min.*, 1931, **15**, 74.
[78] *Physical Rev.*, 1930, [ii], **35**, 509; **36**, 57; 1931, [ii], **37**, 481; *A.*, 1930, 1234.

distance that their maxima $\psi\bar{\psi}$ (electric density) coincide, while in the case of ionic compounds repulsive forces prevent ions approaching closer than to a point where their density is about 10% of the maximum. In the second paper he suggested that exchange and ionic phenomena both take part in very different degrees in different metals, and thus arrived at a reasonable value for the interatomic distance of sodium.

Pauling [79] has developed the case of homopolar binding in much greater detail. The theory cannot be discussed here, but some of its most important contributions to crystal structure may be mentioned. By means of it, he is able to predict the direction and strengths of bonds formed between atoms sharing *s*, *p*, or *d* electrons. He concludes that "*p* electrons will form stronger bonds than *s* electrons," and that "the bonds formed by *p* electrons in an atom tend to be oriented at right angles to one another." This accounts for the electric moment of water and ammonia, and also for the curious square As_4 group in $CuAs_3$. In certain cases the O–H bond may be electronic. "An atom, in which only *s* and *p* eigenfunctions contribute to bond formation and in which the quantisation in polar co-ordinates is broken, can form one, two, three, or four equivalent bonds, which are directed toward the corners of a regular tetrahedron." This accounts for the tetrahedral carbon atom with free rotation about single, but not about double, bonds, and the tetrahedral AX_4 groups, and also explains the pyramidal SO_3, ClO_3, etc., configurations (see Slater),[80] and the kinked NO_2' ion. In special cases, 3 *s* bonds may make larger angles, as in NO_3,CO_3, and graphite. With *d* electrons more variations are possible, "with a single *d* eigenfunction no more than four strong bonds can be formed, and these lie in a plane" as in the $PtCl_4''$ ion, "but if three *d* eigenfunctions are available, stronger bonds directed toward tetrahedron corners can be formed," as CrO_4'', while "if two *d* eigenfunctions are available, six equivalent eigenfunctions can be formed. These form strong bonds, of strength 2·923, directed toward the corners of a regular octahedron" as in $PtCl_6''$ or towards those of a hexagonal prism as in MoS_2. Besides the prediction of bond directions and strengths, magnetic moments can be predicted or used as a criterion for the nature of bonds in complex structure.

Ionic and Atomic Radii.—The two types of bond, homopolar and ionic, have been shown by quantum mechanics to pass continuously into each other. For purposes of crystal analysis the distinction between bond types, in limiting cases such as the silver halides, is

[79] *J. Amer. Chem. Soc.*, 1931, **53**, 1367; *A.*, 670; *Physical Rev.*, 1931, **37**, 1185.

[80] See J. C. Slater, *ibid.*, **38**, 325.

not a practical necessity. For the prediction of interatomic distances and co-ordination, the concept of ionic radius and co-ordination is quite satisfactory in the great majority of cases, even where it is known that other forces are involved. The utility of this conception is only doubted outside the ranks of crystal structure workers by those who do not appreciate how far it has developed from the conception of a rigid hard ion to one whose size depends in a calculable way on the forces acting on it. Further, ionic sizes can be substantiated quite apart from crystallography by pure quantum mechanical calculation of electron distribution in atoms, and from calculations of lattice energy.

W. H. Zachariasen [81] has prepared a new table of empirical radii of ions of the inert-gas type. To apply these to ordinary crystals they must be corrected for co-ordination number, Coulomb force, and radius ratio. They are given as radii of corresponding univalent ions for the co-ordination number 6. Zachariasen bases his work on the fundamental Born equation

$$\Phi = Az_1z_2e^2/R + B/R^n$$

Φ is the lattice energy, z_1 and z_2 the charges on the ions, R the distance between them, A is the Madelung constant depending on the crystal structure, B the Born repulsion constant, and the index n has values 5, 7, 9, 10, 12 for ions of the He, Ne, A, Kr, and X type respectively. From this he is able to find that approximately

$$R_{12}/R_8 = R_9/R_6 = R_6/R_4 = R_3/R_2 = \sqrt[n-1]{1{\cdot}391},$$
$$R_{12}/R_9 = R_8/R_6 = R_4/R_3 = \sqrt[n-1]{1{\cdot}296}.$$

(The subscripts here refer to co-ordination numbers.)

The correction for valency is carried out by the approximate equation $R_{z_1z_2} = R_{11}/\sqrt[n-1]{z_1z_2}$, where $R_{z_1z_2}$ is the actual interionic distance between ions of charge z_1, z_2, and R_{11} the standard univalent ionic radius.

No correction for radius ratio is attempted; this is negligible except when anions are in contact as in lithium chloride, sodium sulphide, etc., where it leads to increase of interionic distance. But the estimate of the amount depends on a complete knowledge of the crystal energy.

The table of ionic radii thus obtained is semi-empirical in so far as it bases itself on the values 1·33 and 1·81 Å. for K˙ and Cl′, but in 60 out of 81 cases it predicts an interatomic distance to within 0·02 Å. of the observed, and the nine cases when the difference is greater than 0·05 all contain large ions of Br′, I′, S″, Se″, and N‴, which are certainly in contact.

[81] *Z. Krist.*, 1931, **86**, 137.

To extend the theory of rare-gas type ions to those of the transition metals is much more difficult, because here the apparent ionic radius varies much more with the type of compound. Goldschmidt [82] has made a beginning in the case of the first row of B group metals Cu^+ (7·69), Zn^{++} (17·89), Ga^{3+} (30·58), Ge^{4+} (45·50), As^{5+} (62·4), Se^{6+} (81·4), comparing them to the corresponding Na^+ (5·12), Mg^{++} (14·97), Al^{3+} (28·32), Si^{4+} (44·95), P^{5+} (64·74), S^{6+} (87·67). The figures in the brackets represent the ionisation potentials in volts; it will be seen that, whilst $Cu^{I} > Na^{I}$, $Se^{VI} < S^{VI}$, whereas $Si^{IV} \approx Ge^{IV}$. According to Goldschmidt, other things being equal, a greater ionisation potential will lead to a decrease in interatomic distance, particularly with polarisable anions (presumably due to greater exchange probability). Thus while the apparent radius of the transition-metal ions in fluorides is, in general, greater than that of the corresponding inert-gas ion, yet in sulphides, bromides, and hydroxides, etc., they will be larger for arsenic and selenium, equal for germanium, and smaller for gallium, zinc, and copper. The practical equivalence of gallium and aluminium, germanium and silicon, is shown to have wide geochemical importance.

The case of the atomic radii of metals is even more complex. W. Hume-Rothery [83] has put forward an interesting semi-empirical relation $d = n(1/aZ)^x$ between d, the interatomic distance of a metallic element, and n the quantum number of the last closed shell; Z is the atomic number, a is a constant depending on the valency, and x is approximately $\frac{1}{3}$. This equation gives a surprisingly good agreement with observation. Other relations between ionic and atomic diameters have been suggested by E. Herlinger.[84]

The work of Niggli and his school [85] (see *Ann. Reports*, 1930, **27**, 289) lies outside the main course of crystal chemistry. Avoiding the hypothesis of atomic size, they concentrate on the interatomic distances and the space pattern formed by the atomic centres. In this sense, it is a logical development of Weissenberg's theories, but, owing to its geometrical rather than physical point of view, it has not so far found much application in practice. Its undoubted value is diminished by an extremely elaborate and prolix presentation.

Apart from the development of existing theories, the past two years have seen the emergence of the ideas of molecular rotation and

[82] *Norsk Geol. Tidsskr.*, 1931, **12**, 247.

[83] *Phil. Mag.*, 1930, [vii], **10**, 217; *A.*, 1930, 1233.

[84] *Z. Krist.*, 1931, **80**, 465.

[85] P. Niggli, *ibid.*, 1930, **74**, 375, 502; **75**, 228; 1931, **76**, 235; **77**, 140; P. Niggli and F. Laves, *ibid.*, 1930, **73**, 381; 1931, **78**, 208; P. Niggli and E. Brandenberger, *ibid.*, **79**, 379; F. Laves, *ibid.*, 1930, **73**, 202; **76**, 277; T. Ito, *ibid.*, 1930, **73**, 357.

the hydrogen bond, which have thrown much light on obscure and controversial questions of crystal structure.

Molecular Rotation in Crystals.—An anomaly in the entropy of solid hydrogen, led Pauling [86] to consider the possibility of movement of molecules in crystals. A molecule in a crystal is not fixed; considered as a rigid body, it can move about an equilibrium position, and will do so with greater energy at higher temperatures. But if the energy is such that the amplitude of these vibrations approaches $\pi/2$, there is the possibility of the molecule turning end for end, and with further increase of energy the vibration may pass into rotation if the cohesion of the crystal is maintained.

Wave mechanics do not give a sharp criterion between vibrational and rotational motion. At every temperature there is always a possibility of the molecule turning end for end. Nevertheless, a practical criterion can be found separating the two states. If n is the quantum number of the vibration of the molecule, there will be vibration or rotation according as

$$n_0 + 1 < \text{ or } > 2\pi(IV_0)^{\frac{1}{2}}/h$$

where I is the moment of inertia and $2V_0$ is the total change of potential of the molecule passing from a position of stable to unstable equilibrium in the crystal. This expression can be approximately evaluated from specific-heat and band-spectrum data, giving the following values of $n_0 + 1$ and V_0 :

	I_2.	N_2.	O_2.	CO.	CH_4.	HCl.	HBr.	HI.	H_2.
$n_0 + 1$	350	7·0	8·5	7·1	1·6	10·7	10·5	11·1	<0·4
V_0, cals./mol.	25000	450	600	500	90	1700	1300	1200	<56
T (Abs.) transition		35·4°	43·8°		20·4°	98°	117°	126°	

The value of $n_0 + 1$ for hydrogen shows that even at absolute zero the molecules are rotating, while for iodine rotation will not take place in the solid at all, as $n = 12$—15 at the melting point. In the other cases the transition takes place at a definite temperature or temperatures below the melting point. These transitions have long been observed as maxima in the specific-heat curve and are now explained for the first time. (For further theoretical treatment, see T. E. Stern.[87])

This brilliant theory has already received confirmation in many fields. From the equation we may expect rotation when the moment of momentum I of the molecule or the potential V of the directing forces is small. This will occur, not only for molecules, but for ions and radicals movable about bonds permitting free rotation. Pauling had already predicted that in the structure occurring in

[86] *Physical Rev.*, 1930, [ii], **36**, 430; *A.*, 1930, 1357.
[87] *Proc. Roy. Soc.*, 1931, [*A*], **130**, 551.

the high-temperature form of the ammonium salts, with transition temperatures for: NH_4I (− 42·5°), NH_4Br (− 38·0°), NH_4Cl (− 30·4°), the $NH_4^{\cdot}$ ions are rotating and to be considered as spheres rather than tetrahedra. Similar examples have since been found for more complex ions. Ammonium nitrate, for instance, has been found by F. C. Kracek, S. B. Hendricks, and E. Posnjak [259] to have five forms: a rhombic form, $T < -50°$, with both $NH_4^{\cdot}$ and NO_3' fixed; another $T < 32°$, with $NH_4^{\cdot}$ rotating and NO_3' fixed; a monoclinic form, $T < 125°$; a tetragonal with NO_3' rotating about the normal to the plane of the ions; and finally the high-temperature cubic form, $T > 125°$, isomorphous with sodium chloride where both $NH_4^{\cdot}$ and NO_3' are rotating freely. Similar effects have been observed in sodium nitrate [260] and sodium sulphate.[275] In general, the more symmetrical high-temperature polymorphs of inorganic salts such as sodium sulphate and potassium chlorate [267, 268] probably are due to complete or partial rotations.

The difficulty of placing hydrogen atoms in hydrated or co-ordination compounds is largely removed by this conception. Ammonia and water are, for instance, often found on triad or tetrad axes of symmetry too high for their intrinsic symmetry, *e.g.*, in $Co(NH_3)_6Cl_2$ and alum. In all these cases the true symmetry of the radicals is infinite owing to rotation. Rotation will always take place about single bonds unless hindered by stereochemical considerations. Similarly, in the high-temperature form of tridymite and cristobalite, the oxygen atoms probably do not lie anomalously in the straight line between two silicon atoms, but rotate about it at a small distance. One of the most interesting applications of the idea of rotation is in the settling of the controversy on the form of aliphatic chains (see Report for 1928). Examination of paraffins and fatty acids pointed to a zigzag chain of carbon acids, while in that of long-chain amine halides the carbon atoms lay on tetrad axes and seemed necessarily collinear. This is now shown to be due to rotation about an axis parallel to the chain length. S. B. Hendricks [489] has shown, by repeating his experiment at liquid-air temperatures, that a larger cell appears, pointing to a zigzag chain at rest. On the other side, A. Müller [470] has shown, by heating paraffin crystals to within a few degrees of the apparent melting point, that while the cell remains unchanged, the disappearance of certain X-ray reflexions points to rotation of the molecules about their long axes (see p. 305).

The Hydrogen Bond.—The position of hydrogen atoms has always been a great difficulty in crystal structure. They are too light to affect the intensities of X-ray reflexion, yet they obviously occupy space and play a considerable part in the dynamics of the structure.

The rotation of molecules and radicals furnishes one explanation of the failure to fit them into crystal structure. More important is the conception of the hydrogen bond postulated by Huggins, appearing more and more frequently to explain *X*-ray crystal analyses and finally given a theoretical explanation by Pauling.[79] The bond is not covalent but ionic. With atoms of large electron affinity (fluorine, oxygen, and possibly nitrogen) the hydrogen atom may lose its electron and become a small positive ion which, therefore, has the co-ordination number two, and can thus form the group $[F'H^{\bullet}F']'$ or $[O''H^{\bullet}O'']'''$. Such groups have long been recognised in crystals : the former occurs in all acid fluorides. For the latter, two cases occur. If, as in magnesium hydroxide, the sum of bond strengths (see Report for 1929) reaching the oxygen atom is 1, we may safely assume an (OH) group, with the proton inside the oxygen atom. If, however, as in potassium dihydrogen phosphate,[282] staurolite, $Fe(OH)_2,Al_4Si_2O_{10}$, apophyllite,[392] $H_8KCa_4Si_8O_{20}(OH)_8F$, and lepidocrocite, FeO(OH), the sum of bond strength is $\frac{2}{3}$, occurring twice for each hydrogen, we must expect a $[O''H^{\bullet}O'']'''$ group. This will occur most easily when the oxygen atoms are attached to highly charged small positive ions. We may say, therefore, that in anhydrous acids and acid salts, hydrogen behaves like a positive ion ; otherwise it is attached by a covalent link to oxygen and appears as hydroxyl ion. (In acid hydrates the hydrogen bond may be broken by the formation of oxonium ions, $OH_3^{\bullet}$.) Apart from structural evidence, the hydrogen bond is also suggested by Raman spectra.[88]

It is impossible to give any account of the crystal structures analysed in the past two years. Instead, a fairly complete list is appended giving both new crystal types established and substances belonging to well-recognised crystal types. What follows is in the nature of a commentary on this list, stressing the chemical and systematic rather than the geometrical and crystallographic aspects. For this reason, few axial lengths are given and only the shape and symmetry of ions and molecules are considered.

Metallic Crystals.—The classification of metallic and semi-metallic structure has progressed much in the last years and is now fairly complete except for our lack of knowledge of the compounds of the alkali and alkaline-earth metals.[77, 89] These being omitted, metallic and semi-metallic substances so far studied can be classified into four main groups : TT′, TM, TD, MM′, where T stands for a transition element including copper, silver, and gold ; M for a metal

[88] C. Kasper, *J. Amer. Chem. Soc.*, 1931, **53**, 2424; *A.*, 893.

[89] U. Dehlinger, *Ergebnisse der Exakten Naturwissenschaften*, 1931, **10**, 325; J. D. Bernal, *Ergebnisse der Technischen Röntgenkunde*, 1931, **2**, 200; *Metallwirt*, 1930, 983; M. Neuburger, *Z. Krist.* ,1931, **80**, 103; *A.*, 1217.

or semi-metal of the other B sub-groups including (Mg), Al, Si, P, and S, but excluding the halogens, and D is one of the first-row elements, H, B, C, N.

TT′ is represented by the transition metals themselves, their extensive solid solutions with each other and their compounds. The great majority of these are face-centred, body-centred, or hexagonal close-packed in structure, and only differ from solid solutions by the arrangements of the atoms of their components regularly with respect to each other, thus acquiring electrical and mechanical properties more like those of pure metals than alloys. This has been particularly well studied in the case of AuCu and $AuCu_3$ by U. Dehlinger [126] and K. Oshima and G. Sachs,[125] and for AgPt and $AgPt_3$ by C. H. Johannson and J. O. Linde.[127]

The allotropy of metallic elements has been much studied by *X*-rays.[89] The transformations of thallium, cobalt, and manganese have been fully confirmed, and new allotropic phases have been found for chromium, tungsten, nickel, and rhodium. In all these cases, however, it is not quite clear that the possibility of subhydrides has been excluded, which might account for the complicated structures observed.

The TD or interstitial compounds of the transition metals with hydrogen, boron, carbon, or nitrogen, practically unknown three years ago, have now been so thoroughly studied, principally by G. Hägg,[140, 143] that it is possible to form a general picture of their constitution. Nearly all fall into six groups 12a,4, 12b,4, 8a,4, 12a,6, 12b,6, 8b,6, in Hägg's notation, in which the metal atoms are respectively cubic face-centred (12a), body-centred (8a), hexagonal close-packed (12b), or simple hexagonal (8b) lattices with the non-metallic atoms (or in some cases atom pairs C_2,H_2) in the interstices between 4 or 6 metal atoms. The metallic lattice thus formed differs little from that of the pure metal with a slightly larger lattice parameter and greater cohesion, and often with a slight distortion to lower symmetry. The kind of structure seems to depend primarily upon the relative size of the inserted atoms. Where this is too large, as in Fe_2B, FeB, FeSi, Fe_2P, more complicated structures result. S. B. Hendricks and P. B. Kosting [162] have determined the structure of several of these compounds. In all of them, the co-ordination of metal atoms about the non-metal is preserved. Of particular interest are the compounds of the iron–carbon system. The structure of the unstable tetragonal martensite has been studied in detail by E. Öhman,[144] and its formation from austenite (γ-iron) and breakdown into ferrite (α-iron) and cementite (Fe_3C) have been studied on single crystal specimens by G. Kurdjumov and G. Sachs.[145]

The details of the cementite structure have been determined by S. B. Hendricks [146] and by S. Shimura.[149] They differ only in the position of the carbon atoms. According to the more probable structure of Hendricks, the carbon atoms lie between distorted octahedra of iron atoms which themselves occupy positions intermediate between face-centred and body-centred co-ordinations.

For TM compounds, recent work has extended and confirmed Hume-Rothery's rules (*Ann. Reports*, 1929, **26**, 289). The character and crystal structure of the compound are determined by the ratio of electrons to atoms, counting electrons from the last completed shell of Ne(10), Ni(28), Pd(46) (the eighth-group metals themselves counting as zero). As the ratios get larger, the character of the compound becomes less and less metallic : Ratio 3 : 2, body-centred cubic or β-Mn structure; 21 : 13, γ-structure; 7 : 4, close-packed hexagonal; 5 : 2, NiAs structure; 4 : 1, FeS_2 structures (pyrite and marcasite). This illustrates quantitatively the natural expectation that the greater the proportion of the metalloidal element or the higher its group the greater the departure from metallic character of the resulting compound.

The most curious of these ratios and structures (that of the 21 : 13, γ-structures) has been extended to the compounds of the eighth group. A. Westgren and W. Ekman [165, 166] have prepared alloys X_5Zn_{21}, where X = Fe, Co, Ni, Rh, Pd, Pt, and Ni_5Cd_{21}, all with one or other of the varieties of γ-structure. A. J. Bradley and C. H. Gregory,[168] on the other hand, have made an exhaustive study by means of *X*-ray intensities of Cu_5Cd_8 and Cu_5Zn_8, and have found that, although the atomic positions are essentially the same in these structures, the different kinds of atom are not similarly distributed in the two cases studied. Electron number seems to dictate the structure chosen; individual atomic positions are determined quasi-statistically by considerations such as atomic size.

The compounds of the heavy B-group metals, Hg, Tl, Pb, Bi, are in general different from those of the elements in corresponding groups: CuHg, for instance, forms a γ-structure but with the proportion of electrons 19 : 13 instead of 21 : 13.

Nothing new has been found about the structures of the B-group metals, but an important generalisation has been pointed out by Hume-Rothery.[90] Except for the heavier elements, all B-group elements have structures in which each atom has $(8-N)$ nearest neighbours where N is the group number of the element. Thus, in Br^{VII} each atom has one neighbour, in Se^{IV} 2, in As^{V} 3, in Ge^{IV} 4, in Ga^{III} 5, and finally in Zn^{II} 6. This is clearly a consequence of the partially homopolar nature of the binding in these cases.

[90] W. Hume-Rothery, *Phil. Mag.*, 1930, [vii], **9**, 65; *A.*, 1930, 279.

Several MM′ systems have been studied, but except for simple rock-salt structures such as SnSb, none of their structures has been worked out. More, however, has been done on sulphides. The marcasite structure has been found by M. J. Buerger[206] to be essentially similar to pyrites, formed of S_2 groups co-ordinated with 6Fe. Argentite, acanthite, chalcocite (Ag_2S and Cu_2S)[204] have been shown to be closely related, but the complete structures have not been worked out. J. W. Gruner[203] has written a very complete account of present knowledge of the structure of sulphides and sulpho-salts.

As in previous years, more of crystal structure work has been done on ionic compounds than on all other substance types put together. Nearly all the structures found, however, agree with the picture of structure as elaborated by Bragg, Goldschmidt, and Pauling, and in a great number of cases the structures themselves may be predicted by Pauling's rules (see *Ann. Reports*, 1929, **26**, 295) and need only have the atomic positions checked by *X*-ray analysis. As before, we will divide them somewhat arbitrarily into five sections: (1) simple ionic oxides and halides, (2) salts with polyatomic ions, (3) hydrated salts and co-ordination compounds, (4) complex oxides, hydroxides, basic and mixed salts, (5) silicates.

(1) *Simple Halides and Oxides.*—E. Zintl and A. Harder[208] have analysed the structures of all the alkali hydrides. These, unlike the transition-metal hydrides (see p. 293), are plainly ionic in character and have a sodium chloride structure. The lattice dimensions *a* (in Å.) are: LiH, 4·084; NaH, 4·880; KH, 5·700; RbH, 6·037; CsH, 6·376. The radius of the hydrogen ion H′ is 1·36—1·54 Å., thus lying between fluorine (1·31) and chlorine (1·81), though nearer the former, so that mixed crystals can be formed between LiH and LiF. The alkali cyanides studied by G. Natta and L. Passerini[209] are also isomorphous with the halides: the radius of CN′ may be taken as 1·92, lying midway between that of Cl′ (1·81) and that of Br′ (2·00). Thus we have the sequence of univalent negative ions: F, H, Cl, CN, Br, I.

Apart from this, the chief advance here has been the elucidation by F. Ebert, H. Bräkken, and N. Wooster of the structure of AX_3 compounds, particularly difficult on account of their hygroscopic properties. Most of the halide structures lately studied are found to be based on a close packing of halogen ions and thus resemble each other in lattice dimensions and general character. Thus, referring them to hexagonal axes, we have:

	LiCl.	$MgCl_2$.	$CrCl_3$.	$FeCl_3$.
a	6·28	6·20	6·02	5·92
c	17·8	17·3	17·3	17·3

In all these cases the metal ions lie between six Cl′ ions, the difference being that in the first case the Cl′ ions are similarly surrounded by six Li˙ ions, while in others, owing to the higher polarising power of the kations, the Cl′ ions have three or two kation neighbours on one side only, giving rise to layer lattices. Where the valencies of the kations are different, mixed crystal formation can even take place, as between LiBr and $MgBr_2$.

The fluorides have structures different from those of the other halides but they are also based on close packing. In the halides of the heavy metals, lead chloride and mercuric bromide, F. D. Miles,[221] M. Mathieu,[222] and H. J. Verweel and J. M. Bijvoet [223] have shown that there is a tendency to form definite molecules, so that these are strictly only semi-ionic compounds. The tetrahalides are also molecular (see p. 303).

Among oxides, the structure of the C group of the sesquioxides, of which bixybite is the type, is particularly interesting, as it is the first case where two alternative structures are absolutely indistinguishable by *X*-ray methods. The structure consists of (FeMn)˙˙ ions in a slightly distorted cubic close packing, each surrounded by a much more distorted O″ octahedron. The metal atoms are fixed by a parameter, a change of sign of which does not affect the *X*-ray intensity. L. Pauling and M. D. Shappell [235] find that the negative value gives reasonable interionic distances, whereas the positive value originally chosen by W. Zachariasen [236] does not. Chromic, molybdic, and tungstic anhydrides, studied by H. Bräkken [242] and W. A. Wooster [240] and N. Wooster,[241] are not isomorphous. The second appears to be a larger lattice based on molybdenum–oxygen octahedra sharing edges. The third, although triclinic, approximates to a cubic structure of side 3·75 Å., with the tungsten atoms at the corners and the oxygen atoms halfway along the edges.

(2) *Anhydrous Salts.*—The chief interest in the structure of salts with complex ions lies in the light that can be thrown on the size and shape of the ions. These may now be classified as follows: linear ions, XX, XY, XYZ, BX_2; straight or angular, planar ions BX_3; tetrahedral or square ions BX_4; octahedral ions BX_6. Of the first type the carbides or more properly the acetylides have been shown by M. von Stackelberg [244] to be ionic compounds of (C⁝C)″ or (H·C⁝C)′, forming tetragonal crystals and showing evidence of belonging to a cubic (rotating ?) form at higher temperatures. He has also shown [245] that the hexaborides CaB_6, SrB_6, etc., have a CsCl structure of Ca and B_6, the latter an octahedron of boron atoms. This is very difficult to understand in terms of either ionic or homopolar binding. The azides, NNN′, [246–248] have straight

ions, but the nitrites, $O^{N}O$, and chlorites, $O^{Cl}O$, have been definitely shown by G. E. Ziegler [251] and G. R. Levi and A. Scherillo [250] to have angular ions according to the predictions of Zachariasen [252] and Slater [80] (see *Ann. Reports*, 1929, **26**, 301).

Sodium sulphite and lithium iodate, which have been very carefully studied by Zachariasen,[253, 254] show pyramidal AX_3 groups; the latter may even be considered as a mixed oxide, $Li^{I}I^{V}$ and O_3^{II}.

The very interesting group of fluocarbonates studied by I. Oftedal[264] have been shown to be based on a hexagonal net of $[Ce_n(La, Nd, etc.) F_n]^{2n+}$ of side 4·09 Å. as in the trifluorite tysonite,[226] CeF_3. The CO_3'' groups pack between these layers parallel to the trigonal axes, thus giving rise to positive instead of the negative birefringence of most other carbonates. The close similarity of the hexagonal net of these compounds gives rise to parallel growths and continuous replacement of F_2 by CO_3 in single crystals.

Of AX_4 types, most interesting are the cubic, high-temperature forms of the perchlorates of Na, Ag, NH_4, K, Rb, Cs, and Tl, studied by K. Herrmann and W. Ilge [267] and by H. Bräkken and L. Harang,[268] which are essentially of sodium chloride type. In this case also the high symmetry may be due to rotation or oscillation of the group ClO_4'.

Potassium dihydrogen phosphate has been investigated by J. West [282] with an elegant application of the Fourier method avoiding all *a priori* assumptions of scattering power, extinction, etc. In this way an almost regular tetrahedron is found for the PO_4 group, of 2·46—2·6 Å. side. The distribution of the tetrahedra with respect to each other and to the potassium ions strongly suggests a hydrogen bond between neighbouring PO_4 groups, so that the formula might be written

```
     H    H
     O    O
 ··HOPOHOPOH···
     O    O
     H  K H
     O    O
 ··HOPOHOPOH···
     O    O
     H    H
     ⋮    ⋮
```

The structure of apatite, the leading member of an important group of mineral phosphates, has been fully worked out by S. von Náray-Szabó [283] and M. Mehmel,[284] who agree in essentials. It is an excellent example of the influence of crystal structure on the very existence of compounds. To form $Ca_3(PO_4)_2$ crystals seems

to involve a geometrically difficult arrangement of atoms, for it is never formed in nature or artificially. Instead $[Ca_5(PO_4)_3]^{\cdot}$ balances its electric charge by the addition of one halogen atom which lies between three calcium atoms on triad axes, so that the formula may be written $(Ca_3F)\cdot Ca_2(PO_4)_3$.

(3) *Hydrated Salts, etc.*—As the result of recent work, the rôle of water of crystallisation is becoming clearer.[91] Where water is found in a crystal, apart from hydroxyl groups decomposed only at high temperatures, it can occur in a variety of ways: (1) As isolated molecules or chains of molecules in holes in a firm structure (zeolitic water); here it can be removed and replaced without destruction of the crystal. (2) In sheets separating anhydrous sections of the crystal; the classical case is gypsum. (Here is an interesting case of isomorphism between gypsum, $CaSO_4,2H_2O$, brushite, $CaHPO_4,2H_2O$, and ardealite, $Ca_2HPO_4SO_4,4H_2O$.)[299] (3) Co-ordinated as tetrahedra, octahedra, etc., around definite atoms in the structure $K_2[Mg(OH_2)_6](SO_4)_2$. (4) Possibly in the case of polyhydrates a continuous ice structure exists, in the holes of which the ions are placed.

Two important examples of isomorphous series of hydrates have been analysed in the last two years. The structure of $NiSnCl_6,6H_2O$, studied by Pauling, [304] is that of the large series of the general type $A^{II}B^{IV}X_6,6H_2O$ (or $6NH_3$), where A can be Mg, Mn, Zn, etc., B is Si, Sn, Pd, Pt, etc., and X is F, Cl, Br, I. The structure is essentially a body-centred cubic cæsium chloride structure, with $[A^{II}6H_2O]^{+2}$ for Cs and $[BX_6]^{-2}$ for Cl. The water or ammonia molecules and the halogen atoms form almost regular octahedra round the metal atoms, but the larger size of the last lead to distortion to rhombohedral symmetry.

W. Hofmann [306] has analysed Tutton's monoclinic double sulphates $M^I_2M^{II}XO_4,6H_2O$, where M^I is K, NH_4, Tl, etc., M^{II} is Mg, Zn, Cd, etc., and X is S, Se, etc.; and by a method of comparing intensities of reflexion between $(NH_4)_2Mg(SO_4)_2,6H_2O$ and $Tl_2Mg(SO_4)_2,6H_2O$, $(NH_4)_2Cd(SO_4)_2,6H_2O$, and $(NH_4)_2Mg(SeO_4)_2,6H_2O$, he has determined the parameters of M^I, M^{II}, and X. The position of the oxygen atoms and water molecules is less certain, but the best fit is obtained by placing the former in the usual tetrahedron round X and the latter in an octahedron round M^{II}.

(4) *Complex Oxides, Hydroxides, etc.*—The mixed oxides and hydroxides do not form a class of their own. They are connected

[91] L. Hackspill and A. P. Kieffer, *Ann. Chim.*, 1930, [x], **14**, 227; *A.*, 1930, 1535; F. J. Garrick, *Phil. Mag.*, 1930, [vii], **9**, 131; *A.*, 1930, 276; A. Seyewetz and Brissaud, *Compt. rend.*, 1930, **190**, 1131; *A.*, 1930, 872; W. H. Keesom and H. H. Mooy, *Nature*, 1930, **126**, 243; *A.*, 1930, 1233.

by isomorphous relations to the simple oxides (Fe_2O_3, hematite; $FeTiO_3$, ilmenite), to the complex-ion salts (Ag_2MoO_4; Al_2MgO_4, spinel) and to the silicates (Mg_2SiO_4, olivine; Al_2BeO_4, chrysoberyl). Their distinguishing character is their heterogeneity and the absence of highly charged small positive ions, so that no electrostatic valencies higher than 1 exist throughout the structure.

They may be classified by means of the kation oxygen (hydroxy-fluorine) co-ordinations found in them. These co-ordinations range from 4 (only in spinels and allied structures) to 6, which is the rule for most of the following kations : Sb^{5+}, Nb^{5+}, Ta^{5+}, Ti^{4+}, Sn^{4+}, Al^{3+}, Sc^{3+}, Ga^{3+}, Cr^{3+}, Fe^{3+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Li^{+} ; 6—8 for Zr^{4+}, Hf^{4+}, Ce^{4+}, U^{4+}, Th^{4+}, (Sm^{3+}. . . . Cp^{3+}), Y^{3+}, Ca^{2+}, Cd^{2+}, Na^{+}; and 8—12 for (La^{3+}. . . . Sm^{3+}), Sr^{2+}, Ba^{2+}, Pb^{2+}, K^{+}, Rb^{+}, Cs^{+}.

The following seven types of structure have been observed :

$[A_2]^6[B]^4O_4$ Spinel; $[A]^6[B]^6O_3$ Ilmenite;
$[A_2]^6[B]^6O_5$ Pseudobrookite; $[A]^6[B_2]^6O_6$ Columbite;
$[A_2]^{6-8}[B_2]^6O_7$ Pyrochlorite; $[A_2]^{8-12}[B]^6O_3$ Perovskite;
$[A_3]^8[B_2]^6[C_3]^4O_{12}$ Garnet.

A and B may be any of the metals of the above list, with the restrictions that the co-ordination rules be observed and that the positive charge of the kations is exactly balanced. This can be done by adjusting the charges between the A and the B atoms by such replacements as Nb^{5+}, Fe^{2+}, by Ti^{4+}, Fe^{3+}, or, where the total charge is deficient, by the replacement of oxygen by hydroxyl or fluorine, so that, for instance, the general formula for a pyrochlorite may be written

$$[a_4A^{4+}/a_3A^{3+}/a_2A^{2+}/a_1A^{+}]^6[b_5B^{5+}/b_4B^{4+}/b_3B^{3+}]^6/xO/y(OH)/zF$$

where $a_4 + a_3 + a_2 + a_1 = 2$; $b_5 + b_4 + b_3 = 2$; $x + y + z = 7$; and $4a_4 + 3a_3 + 2a_2 + a_1 + 5b_5 + 4b_4 + 3b_3 = 2x + y + z$.

The spinels are still providing most material for study. Many new examples of this already large group have been found, including such unexpected compounds as $CuAl_2O_4$, $MgGa_2O_4$, Ni_2GeO_4, and Zn_2SnO_4. In last year's Report on Geochemistry, critical remarks were made on the indefinite formulæ given by *X*-ray workers to spinels. Unfortunately, this indefiniteness is due to Nature. The spinel cell is a definite entity, a cube of side 8·1—8·5 Å., containing 24 metal atoms and 32—36 oxygen atoms. Any spinel can, however, always be considered a mixed crystal between true spinel, A_2BX_4, and γ-Al_2O_3, or magnetic Fe_2O_3. The structure of the last has been determined by J. Thewlis [328] from intensity measure-

ments. The four extra oxygen atoms are placed in positions preserving an Fe–O distance of 1·9 Å.; otherwise the structure is that of spinel. The accepted spinel structure has been questioned by F. Machatschki [329] and T. F. W. Barth and E. Posnjak [330] in different senses. Machatschki, by changing the oxygen parameters from 0·375 to 0·384 in $MgAl_2O_4$, and making the aluminium octahedra tighter and the magnesium tetrahedra looser, gets both better agreement with intensities, and interatomic distances more in accord with modern views. Barth and Posnjak, on the other hand, propose, from the study of $MgGa_2O_4$ and $MgFe_2O_4$, the more radical change of half the Ga($Fe^{\cdot\cdot\cdot}$) atoms to the tetrahedral positions, leaving the remainder of the MgGa($Fe^{\cdot\cdot}$ $Fe^{\cdot\cdot\cdot}$) in statistical distribution over the octahedral positions, so that the spinel formula should be written as (MgAl)AlO_4, and magnetite as ($Fe^{\cdot\cdot}$ $Fe^{\cdot\cdot\cdot}$)$Fe^{\cdot\cdot\cdot}O_4$, whilst Mg_2TiO_4 would remain as before. Both these suggestions may be true, but further work is needed. $CaIn_2O_4$ and $CdIn_2O_4$ [340] belong to the related Mn_3O_4, hausmannite type. On account of its complexity, β-alumina has occupied the attention of *X*-ray crystallographers for some years. W. L. Bragg, C. Gottfried, and J. West [345] have finally decided that it is really an acid aluminate, $Na_2Al_{23}O_{35\frac{1}{2}}$. It may be considered a compound of corundum (aluminium 6-co-ordinated), γ-Al_2O_3 (aluminium 4-co-ordinated), and sodium aluminate, arranged in layers.

The titanates, pseudobrookite, Fe_2TiO_5, and columbite, (Fe,Mn)$(Nb,Ti)_2O_6$, have been analysed by L. Pauling [342] and J. H. Sturdivant [341]; both titanium and niobium are found in 6-co-ordination.

H. R. von Gaertner,[349] F. Machatschki,[356] and E. Brandenberger [357] have investigated complicated niobates and antimonates. Of these, loparite, $(Na,Ca,Ce)_2(Nb,Ti)_2O_6$, appears to belong to the perovskite type with a small cubic cell $a = 3{\cdot}84$ Å., whilst the others, atopite, mauzelite, and koppite, belong to a new type, that of pyrochlorite, also cubic, $a \approx 10$ Å. In this type, $A_2B_2O_7$, A seems to be 6—8-co-ordinated (the oxygen positions are uncertain) and B 6-co-ordinated.

Of complex hydroxides, hambergite, $Be_2BO_3(OH)$, is the only one that has been fully analysed. Zachariasen's work [344] is particularly interesting in showing $B^{\cdot\cdot\cdot}$ always co-ordinated with 3O. The BO_3''' triangles lie parallel to the *c* axis, giving rise to strong positive birefringence.

The oxides and hydroxides of aluminium and iron have been much studied, but no new structures have been advanced. The systems are very complex: there are at least four forms of $Al_2O_3,3H_2O$ distinguishable by *X*-rays.

Some very complex ionic compounds come most naturally into this section. The boleite--pseudoboleite group,

$$x\mathrm{PbCl_2}, y\mathrm{AgCl}. z\mathrm{Cu(OH)_2},$$

has given rise to controversy,[348] but it seems that instead of being cubic they form a related tetragonal group with multiple relation between the axes as in the bastnaesite group (see above).

(5) *Silicates.*—The analysis of the silicate structures and the discovery of their natural classification have been the greatest triumph of *X*-ray crystallography. In the last two years the field has been nearly covered. The structures of all the common silicate types, as well as those of many rarer ones, are now known. W. L. Bragg, who with his school has accomplished most of the work, has given a full account [360] of all silicate structures determined up till now in "The Structures of Silicates" (2nd edtn., 1932), so no description of new structures will be attempted here. Machatschki's classification of silicates has been extended and modified by V. M. Goldschmidt and S. Náray-Zabó. It is based essentially on the mode of binding of tetrahedra of $(SiO_4)^{4-}$ and also of $(AlO_4)^{5-}$, $(BO_4)^{5-}$, $(BeO_4)^{6-}$, $(ZnO_4)^{6-}$, etc. The simple silicates, those containing no other 4-co-ordinated ion, form a series of increasing acidity :

$(SiO_4)^{4-}$, separate tetrahedra (orthosilicates);
$(Si_2O_7)^{6-}$, pairs of tetrahedra with one corner shared (disilicates);
$(Si_3O_9)^{6-}$, ring of tetrahedra [benitoite, $BaTi(Si_3O_9)$];
$(Si_6O_{18})^{12-}$, ring of tetrahedra (not yet found except in the beryllosilicate, beryl);
$(Si_nO_{3n})^{2n-}$, chain of tetrahedra (metasilicates, pyroxenes);
$(Si_{4n}O_{11n})^{6n-}$, band (double chain) of tetrahedra (amphiboles);
$(Si_{2n}O_{5n})^{2n-}$, sheet of tetrahedra (mica, talc, chlorite group), never found in simple silicates.
SiO_2, framework of tetrahedra (tridymite, quartz).

This main sequence can be varied in two ways. With any simple silicate can be combined groups, chains, or sheets of oxides or hydroxides, thus Mg_2SiO_4, olivine, combined with $Mg(OH)_2$ sheets gives the norbergite, clinohumite series; rows of Al_nO_n exist with $AlSiO_4$ in cyanite, and Al_2F_2 groups in topaz, $Al_2F_2SiO_4$. This gives rise to a whole series of basic silicates corresponding to each simple silicate and extending to cases such as talc, $MgSi_2O_5,2Mg(OH)_2$, where the simple silicate $MgSi_2O_5$ is not stable. On the other hand, some of the Si^{4+} in a silicate can be replaced by $Al^{3+}(B^{3+},Be^{2+})$, either in stoicheiometric or in indefinite amount, increasing the net charge of the complex ion. Thus, diopside, $CaMg(SiO_3)_2$, gives rise to augite, $(Ca,Na)(Mg,Fe,Al)(Al,Si)_2O_6$, and tremolite to hornblende. With more acid silicates, such as the mica and

felspar group, only aluminosilicates are stable, the first being characterised by sheets of tetrahedra with the ratios $(Si,Al)_2O_5$, the second by various spatial frameworks of formula $(Si,Al)O_2$. In general, beryllo- and boro-silicates resemble aluminosilicates, but some structures can be formed which would be impossible for simple silicates such as phenakite, Be_2SiO_4. A silicate can, of course, be basic, hydrous, and aluminous at the same time, and this is the cause of much of the apparent complexity of silicate formulæ.

Notable work of the past two years includes the structure of the orthosilicates sphene, $CaTiSiO_5$, by W. H. Zachariasen;[363] eulytite, $Bi_4(SiO_4)_3$, by G. Menzer;[362] and the establishing of Si_2O_7 groups in thortveitite, melitite,[367] hardystonite,[368] meliphanite,[369] and vesuvian,[370] and of the $(Si_3O_9)^{6-}$ group in benitoite by Zachariasen.[373] The complete scheme of the monoclinic and orthorhombic pyroxenes and amphiboles has been worked out by B. E. Warren.[376–380] These have all been shown to be derivable from the simplest type, monoclinic pyroxene (diopside). The rhombic pyroxenes are formed by a reflexion of the cell in the (100) plane, the monoclinic amphiboles by a doubling of the *b* axes, and consequently of the silica chains. The rhombic amphiboles arise in turn by reflexion in the (100) plane. The wollastonite, $CaSiO_3$, group is shown to have no relation to the pyroxenes and to be triclinic instead of monoclinic as had been previously supposed.[376]

The study of the mica group has been carried out by Pauling[385] and by W. W. Jackson and J. West.[386] The great variety of platy minerals, micas, brittle micas, chlorites, and talcs, have been shown to be produced by various combinations of hexagonal layers of $(Si_{4n}O_{10n})^{-4n}$, $(Si_{3n}Al_nO_{10n})^{-5n}$, $(Si_{2n}Al_{2n}O_{10n})^{-6n}$, etc., with $Mg(OH)_2$,$Al(OH)_3$,$AlO(OH)$, and neutralised by ions of $K^{\cdot}$, $Na^{\cdot}$, $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, etc. The structure of apophyllite[392] shows it to be an alternative net-like silicate based on square, instead of hexagonal, meshes.

Danburite[399] is a borosilicate closely related to the felspars. The structure of these is not exactly known, but that proposed by F. Schiebold[400] must be near the truth. The zeolites[411–420] have been much studied, especially by Pauling. The frameworks on which these compounds are based seem chiefly of three types. Those based on squares and collapsed octagons (danburite, felspar type), those based on squares and hexagons (cuboctahedra) (ultramarine, sodalite type), and those based on hexagons alone (tridymite, nepheline type). More complex arrangements are found in the fibrous natrolite, scapolite, and helvine groups. *X*-Ray analysis has been used successfully in the study of synthetic silicates and

even of glasses. It will probably become indispensable in these fields. It has already proved that the synthetic amphibole formed in the magnesia–silica system is really olivine.[425]

V. M. Goldschmidt [338] has shown that germanium forms a whole series of compounds isomorphous with all the chief types of silicates (including germanium-olivine, phenakite, and pyroxene), so that in future the study of the silicates must include that of the germanates.

Molecular Compounds.—Enough simple molecular compounds have been analysed to show that fundamentally all have the same structure, that of cubic close packing.[435–450] An exception is para-hydrogen, which is hexagonally close packed. The lattice dimensions of all simple molecular elements and compounds so far determined are set out below (in Å.U.), r being the "effective molecular radius :

	F′.	Ne.	NH_3.	CH_4.	Cl′.	A.	HCl.	H_2S.	H_3P.
a	—	4·52	5·19	5·89	—	5·43	5·50	5·79	6·31
r	1·33	1·60	1·80	2·08	1·8	1·92	1·95	2·04	2·23

	Br′.	Kr.	HBr.	H_2Se.	H_3As.	I′.	X.	HI.
a	—	5·59	5·77	6·05	6·40	—	6·18	6·10 $c=6·6$
r	2·0	1·98	2·04	2·14	2·26	2·2	2·19	2·21

	H_2.	N_2.	CO.	N_2O.	CO_2.	O_2.	NO_2.	I_2.	COS.
a	3·75 $c=6·12$	5·63	5·63	5·73	5·62	Orthorhombic.	7·77 6 mols. per cell.	$a=4·80$ $b=7·25$ $c=9·78$	4·09 $\alpha=98°$
r	1·88	2·00	1·99	2·03	1·99			4 mols. per cell.	1 mol. per cell.

	SiF_4.	$ZrCl_4$.	SiI_4.	GeI_4.	SnI_4.	CHI_3.
a	5·41	10·32 $=2\times5·16$	12·0 $=2\times6·0$	11·9 $=2\times5·95$	12·23 $=2\times6·12$	$a=6·82$ $c=7·52$
	8 mols. per cell.					2 mols. per cell.
Effective radius of halogen	1·51	1·81	2·12	2·10	2·16	2·15

The atomic diameters of the rare gases in the solid state are about 0·75 of that deduced from their gaseous properties, as pointed out by Keesom.[91] It is interesting to notice that the series Ne, –, –, H_3N, H_4C; A, HCl, H_2S, H_3P; Kr, HBr, H_2Se; X, HI, with total electron number 10, 18, 36, and 54 respectively, have structures with only slightly increasing lattice parameters. (The only exceptions are hydrogen fluoride and water, which polymerise.) The other tri- and poly-atomic molecules have similar structures with larger cells and lower symmetry, but in these rotation takes place at higher temperatures. Where the atoms are large, as in I_2, COS, CHI_3, SnI_4, etc., the close-packing of the molecules gives place to that of individual atoms. The case of nitrogen peroxide is still in dispute. L. Vegard [444] finds 6 linear molecules of ONO in a cell,

S. B. Hendricks,[445] from Vegard's measurements, finds 3 plane molecules $\genfrac{}{}{0pt}{}{O}{O}{>}N{-}N{<}\genfrac{}{}{0pt}{}{O}{O}$. Other more complex molecular substances, $Fe_3(CO)_{12}$ [455] and $B_{10}H_{14}$,[456] have been studied but without much information on the nature of the molecules. $Si(OCH_3)_4$, studied by W. Eulitz,[457] shows a regular tetrahedral arrangement of OCH_3 about Si. Particularly interesting is the study of the various forms of sulphur and selenium and their solid solutions by F. Halla, E. Mehl, and F. X. Bosch,[460, 461] pointing in every case to an asymmetrical molecule S_8 or Se_8. Plastic sulphur has been shown by J. J. Trillat and J. Forestier [462] to have a fibrous structure, $a = 9{\cdot}35$ Å.

S. B. Hendricks[468] has given an excellent survey of the present state of knowledge of the structure of organic compounds. The essential difficulty in their analysis is that they are composed mostly of hydrogen, carbon, nitrogen, and oxygen, the first of which gives no *X*-ray reflexion, whilst those of the other three are practically indistinguishable. Some crystals, owing to simplicity or high symmetry, are suitable for complete *X*-ray analysis, but the great majority are not, and need to have their structures elucidated by means of a knowledge of molecular form, interatomic distances drawn from other analyses, Raman spectra, etc., while for the orientation of the molecules, a knowledge of probable interactions of radicals and the information given by cleavage, refractive indices, etc., is needed. Such analyses cannot be used as authoritative except in the one important point of molecular symmetry, which can be indubitably proved by *X*-rays. It is obviously necessary to proceed by a method of systematic research over the whole field, and this has been pushed forward rapidly.

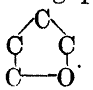
A. Müller [470] has published another important paper on the hydrocarbons. Hydrocarbons of 11, 15, 17—21, 23, 24, 29, and 30 carbon atoms were found to crystallise in the normal state (see *Ann. Reports*, 1928, **25**, 293), those of 5—10, 16, 18, and 20 carbon atoms in another form with smaller *c* spacing. Measurements at liquid-air temperatures and near the melting point show, first, that the coefficients of expansion are very different in different directions, $C_a = 0{\cdot}00017$, $C_b = 0{\cdot}00005$, $C_c < 0{\cdot}00002$, showing that the expansion is nearly entirely due to the temperature affecting the van der Waals forces between hydrogen atoms, the carbon chains exhibiting no measurable expansion. Secondly, the lateral anisotropy is very marked. The expansion is much greater on the *a* direction than the *b*, leading to a closer approximation to hexagonal close packing, as can be seen from the variation of the two shortest intermolecular distances *b* and *D*: at liquid-air temper-

atures, they are 4·9 and 4·35; at room temperatures, 4·9 and 4·46; a few degrees below the melting point, 5·0 and 4·58. Just below the melting point the two different distances give place to one at 4·85, while in the liquid this increases to 5·2 Å. These changes are no doubt due, first, to oscillations of the molecules about their long axes, at higher temperatures to rotations while still in the solid, and finally, to translatory movements in the liquid. N. Fuchs [473] has observed and photographed crystals of $C_{34}H_{70}$ on a liquid surface only 1 molecule thick. The interfacial angles agree exactly with those of Müller's hydrocarbons. The *n*-fatty acids and alcohols have been much studied, particularly by S. H. Piper and T. Malkin,[477] T. Malkin,[483] and J. Thibaut and F. D. La Tour,[479] and unsaturated long-chain compounds by J. Hengstenberg and R. Kuhn.[487, 489]

Of other aliphatic compounds, three groups in particular have been studied in the last two years: (1) the amino-acids, peptides, and compounds containing the group R·CO·NH·R; (2) the sugars; (3) *cyclo*hexane and its derivatives. The amino-compounds, which have been studied in connexion with the attempt to discover the structure of proteins (see this vol., p. 332), are examples of molecular crystals where the chief cohesive forces are electrostatic between the negative carbonyl and the positive imino- or amino-radicals; hence the high densities and melting points. R. W. G. Wyckoff [490] has redetermined the parameters of urea from absolute intensity measurements; it is now one of the most exactly known organic structures. J. Hengstenberg and F. V. Lenel [491] and J. D. Bernal [492] have determined the structure of glycine. The molecules form sheets parallel to the cleavage. There is some evidence that in the solid " zwitter-ions " $\underset{+NH_3}{\overset{H_2}{C}}—C\lt{}^{O}_{O}—$ are formed.

Among other amino-acids studied by the latter are alanine, where the molecules $\overset{+}{N}H_3 \cdot CHMe \cdot \overset{-}{C}O_2$ show a well-marked pseudo-plane of symmetry, and $[CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot S \cdot]_2$, *l*-cystine, where 6 molecules with diad axes of symmetry are arranged in a spiral about a six-fold screw axis. Of ring compounds, diketopiperazine,[492] diethylbarbituric acid,[494] and *spiro*hydantoin [495] have been studied.

The sugars have been studied chiefly by J. Hengstenberg and H. Mark,[496] K. Andress and L. Reinhardt,[501] T. C. Marwick,[498] and E. G. Cox.[502] Cells and space groups can be established, but the difficulties of stereoisomerism and the absence of useful optical indications owing to the preponderance of the hydroxyl effects have prevented any trustworthy determination of structure. Every-

thing points, however, to the existence of an almost plane ring  O. Hassel [504] has shown that *cyclo*hexane is cubic, $a = 8{\cdot}41$ Å., 4 molecules per cell, and the molecule must have ditrigonal scalenohedral symmetry $\bar{3}$. This points to a strainless alternating  ring. His later investigations (with H. Kringstad) [505] of *trans*-1 : 4-dibromo- and -di-iodo-*cyclo*hexane show that these compounds also possess a centre of symmetry. The *cyclo*hexanols have been studied by A. L. Patterson [506] and T. N. White,[506, 507] but the same difficulties occur as in the sugars.

Aromatic compounds have been more studied than ever before, but, except for a few mentioned below, no information is furnished as to molecular structure. The weight of evidence in favour of the plane ring is, however, increasing. (Mrs.) K. Lonsdale [509] has made a determination of the structure of hexachlorobenzene by Fourier analysis. Although the evidence for a flat ring is not as conclusive as in the case of hexamethylbenzene, the chlorine and carbon atoms have been shown to lie in nearly a regular hexagon. (Miss) I. E. Knaggs [510] has shown that hexa-aminobenzene has a trigonal axis. A great number of substituted benzene compounds have been examined by E. Hertel and K. Schneider.[512, 513] In all cases, space groups have been found, but while in some, *e.g.*, trinitroresorcinol, the structure he proposes is in accord with the optical data, in others there are definite contradictions, and in still more there is no evidence. The arguments relied on for suggesting structures depend on considerations of packing, which, though they may lead to correct structures, are not unambiguous. Of the three dinitrobenzenes, *m*- has a plane of symmetry, *p*- a centre, and *o*- is asymmetric. 2 : 4 : 6-Tribromobenzonitrile has a plane of symmetry.

The structure of naphthalene is now fairly well established. The two rings lie in a plane which is slightly tilted to the (100) planes. This orientation, predicted by K. Banerjee [517] from optical and magnetic data, has been accepted by J. M. Robertson [518] and (Sir) W. Bragg, who had found similar atomic positions but had connected them wrongly in molecules, thus arriving at a structure with puckered rings.[516] This is an excellent example of the importance of using optical methods for organic crystals.

The stilbene–azobenzene series has been much studied; the evidence points to a planar straight double ring, $C_6H_5{\cdot}X{\cdot}X{\cdot}C_6H_5$. Graphite seems to be the last product in the condensation of benzene rings. U. Hofmann and A. Frenzel [524] have shown that graphite crystals can be oxidised reversibly to graphitic acid without change

in the prismatic spacings of the lattice (*i.e.*, without altering the benzenoid nets), but with a change in the *c* spacing from 3·4 to 6·9 Å., and then by hydration to 11·3 Å. This is by far the largest reversible change in crystal structure ever observed.

E. Hertel[526–530] has done valuable work in examining a large number of molecular compounds among organic substances. In general, they have cells bearing simple relations to those of their components. The *X*-ray method is coming more and more into use for the identification of organic compounds; it has the additional advantage of giving as well the maximum molecular weight. For instance, K. Brückl[533] has proved the identity of the alkaloids banisterine and harmine, $C_{13}H_2ON_2$, in this way, and it can be applied just as easily to complicated compounds of unknown composition and structural formula.

The application of *X*-ray methods to the study of colloids and fibres and to biological problems is dealt with in another part of this volume (p. 322).

The following is a list of the chief papers on the *X*-ray analysis of crystals published in 1930 and 1931. Papers containing such measurements incidentally and not leading to cell or space group are omitted, and others may have been overlooked. The papers are arranged according to the classification of substances used in the text:

A. *Metallic compounds.* (1) Elements. (2) Intermetallic compounds and systems of transition metals. (3) Interstitial compounds. (4) Compounds of transition and B-group metals, and semi-metals.

B. *Ionic compounds.* (5) Simple oxides and halides. (6) Anhydrous salts. (7) Hydrates and co ordination compounds. (8) Complex oxides and hydroxides. (9) Silicates.

C. *Molecular compounds.* (10) Simple molecular compounds. (11) Long-chain compounds. (12) Other aliphatic compounds. (13) Aromatic compounds.

In each group, compounds belonging to recognised types are given first. These are designated by the letters used for them in the "Strukturbericht." Next comes a list of new or uncertain structures, and finally in the sections on metals a list of systems examined by *X*-rays, whether these contain definite compounds or not.

Asterisks attached to the reference number give some indication of the kind of investigation: ** signifies a complete structure determination giving atomic positions determined by intensity measurements, * a determination giving cell and space group. Absence of a mark usually refers to simple powder photographs.

1. *Metallic elements.*

Known types : *A1.* β-Tl [116*].
A2. Nb [102, 103]; U [107]; α-Fe [111*, 112*].
A3. αTl [116*]; La [101]; Er [102]; β-Cr [104, 105]; Re [109, 110*]; β-Ni [113, 114].
New structures : γ-Cr [105]; β-W [106]; γ-Mn [108]; β-Rh [115].

2. *Alloys of transition elements.*

Known types : *L10.* AuCu [122, 123*, 124, 125*, 126*].
L11. AgPt [127*].
L12. $AuCu_3$ [122, 123*, 124, 125*, 126*]; $AgPt_3$ [127*].
New structures : Au_2Cu_3 [123]; NiMo [136].
Systems : Ag–Cu [117, 118, 119]; Au–Cu [120, 122–126]; Ag–Au [121]; Ag–Pt [127]; Au–Pt [127]; Fe–Ni [132]; Co–Ni [133]; Ni–Cu [131, 129]; Mn–Cu [128, 130]; Mn–Fe [130, 133]; Cr–Ni [134, 135]; Mo–Ni [136].

3. *Interstitial compounds.*

Known types : *12a,4.* TiH, TiH_2, Zr_4H, ZrH, Pd_2H.
12b,4. Ti_2H, Zr_2H, Ta_2H.
8a,4. TaH.[141, 143]
12a,6. Mn_4N, Fe_4N, Mo_2N, W_2N, ScN, TiN, VN, CrN, ZrN, NbN, ScC, TiC, VC, ZrC, NbC, MoC, TaC.[140, 141]
12b,6. Cr_2N, Mn_2N, Fe_2N, Fe_3N, V_2C, Mo_2C, Ta_2C. W_2C.
8b,6. MoN, MoC, WC.[140, 141]
(Hägg's notation : see p. 293.)
New structures : Fe_xC (martensite) [144*, 145*, 147, 148]; Fe_3C (cementite) [146**, 147, 149**]; Fe_2B [159, 160, 161*], FeB, Fe_2P, Fe_2N, Fe_3N [162**]; VC_2, La, Ce, Pr, Nd, C_2, UC_2, ThC_2 [244, 245].
Systems : Pt–He [137]; Pd–H [138]; Fe–N [151–155]; Cr–C [156, 157]; V–C [158], Fe–V–C [158]; Fe–W–C [150]; Fe–B [159, 160]; Ti–C–O [161].

4. *Metallic compounds of B-group metals, semi-metals, and sulphides, etc.*

Known types : *A4.* Si [200]. *A9.* C [201]. *B3.* SiC [202].
B1. SnSb [195]. *B13.* NiS (millerite) [205**]. *C18.* FeS_2 (marcasite) [206**].
(*γ-Structures*) *D82.* Cu_5Zn_8, Cu_5Cd_8 [168**]; Ag_5Hg_8 [172]; Fe_6Zn_{21}, Co_5Zn_{21}, Ni_5Zn_{21}, Rh_5Zn_{21}, Pd_5Zn_{21} [165, 166].
D83. Cu_7Hg_6 [173, 174]; Ni_5Cd_{21} [166].
D84. Pt_5Zn_{21} [166].
(β-Mn *Structure*) CoZn [166]; Cu_5Si [180].

New structures: AgLi, $AgLi_3$[164]; $TiAl_3$[177]; β-CuAl[178]; $Cu_{23}Al_{21}$[179*]; FeSi[181**]; $Cu_{15}Si_4$[180]; Cu_3Sn[182]; Cu_6As,[186] Cu_3As[184, 185]; Au_2Bi[192]; Ag_2S[204]; CdSb, Cd_3Sb_2[194]; BiSe, Bi_2Se_3[197]; Bi_2Te_3[198]; $Cu_3(FeGe)S_4$ (germanite)[207]; Mg_2N_2.[199]

Systems: Cu–Li[163]; Ag–Li[164]; Fe, Co, Ni, Rh, Pd, Pt–Zn, Ni–Cd[165, 166]; Cu–Zn[169]; Ag–Cd[171]; Cu–Hg[173, 174]; Ag–Hg[172]; Ti–Al[177]; Mn–Al[130, 176]; Fe–Al[175]; Cu–Al[178, 179]; Cu–Si[180]; Ag–Sn[189]; Au–Sn[183]; Ni–Bi[190]; Cu–As[184]; Cu–Sb[187]; Cu–Bi[191]; Ag–As, Ag–Sb, Ag–Bi[188]; Au–Sb[189]; Cd–Sb[193, 194]; Sn–Sb[195]; Sn–Bi[196]; Bi–Se, Pb–Bi[197]; Bi–Te[198].

5. *Simple ionic compounds.*

Known types: *B1.* LiH, NaH, KH, RbH, CsH[208**]; NaCN, KCN, RbCN[209*]; ThO.[239]

B2. CsCN[209]. *C3.* Cu_2O[231]. *C9.* SiO_2[237]. *D51.* Fe_2O_3.[234] *D52.* La_2O_3.[235, 236].

C6. $MgBr_2$, $MnBr_2$, $FeBr_2$, $CoBr_2$, MnI_2, FeI_2, CoI_2.[219] *C19.* $CdCl_2$.[217**, 216].

New structures: AgI (above 146°)[213]; AgCN[211*]; $PbCl_2$[221*, 222]; $HgBr_2$[223**]; AlF_3[224]; FeF_3, RhF_3, PdF_3[225*]; CeF_3[226**]; $AlCl_3$[227]; $CrCl_3$[228**]; AsI_3[229*, 230**]; SbI_3, BiI_3[229*]; NiO[232], $(Mn,Fe)_2O_3$ (bixybite) (C-sesquioxides)[235**, 236]; ZrO_2[238]; CrO_3[240*, 242*]; MoO_3[241**, 242**]; WO_3[242*]; Mg_2N_3[199*].

Systems: LiH–LiF[208]; NaCN–NaCl, NaBr, NaI[209]; NaCl–AgCl[210]; CuI–AgI[212]; LiBr–$MgBr_2$[214]; CaF_2–SrF_2[215]; $CaCl_2$–$M^{II}Cl_2$ (M = Co, Fe, Mn, Cd)[215]; $M_1^{II}O$–$M_2^{II}O$, $M_1^{II}(OH)_2$–$M_2^{II}(OH)_2$ (M^{II} = Mg, Ca, Mn, Co, Ni, Zn, Cd)[220]; Fe_2O_3–Cr_2O_3, Fe_2O_3–Mn_2O_3[233]; Th–ThO_2.[239]

6. *Anhydrous salts.*

Known types: *C11.* CaC_2**, SrC_2, BaC_2, La, Ce, Pr, NdC_2[244].

G1. $CoCO_3$[257]; $(Ca,Mn)CO_3$[255]. *G2.* KNO_3[261**]; $SrCO_3$, $BaCO_3$.[258]

H2. $KMnO_4$[269**]. *H3.* $CaCrO_4$[271**]. *H4.* BaWO[273**].

H22. KH_2PO_4[282***].

New structures: CaB_6, SrB_6, BaB_6[245]; $NaHC_2$, KHC_2[244*]; $TlHF_2$[249]; RbN_3[247, 248*]; $Ba(N_3)_2$[248*]; $Pb(N_3)_2$[246]; $Hg(CNO)_2$[246]; NH_4ClO_2*, $AgClO_2$, $Ca(ClO_2)_2$, etc.[250]; $NaNO_2$[251**]; Na_2SO_3[253**]; $LiIO_3$[254**]; $BaCa(CO_3)_2$.[256]

Polymorphism of $NaNO_3$[260**]; KNO_3[262]; $RbNO_3$[263]; $(NH_4)NO_3$[259*].

Fluocarbonates: $RFCO_3$ (bastnaesite), $2RFCO_3$, $CaCO_3$ (parisite), $RFCO_3$,$CaCO_3$ (synchisite), $2RFCO_3$,$BaCO_3$ (cordylite) (R = La, Ce, Pr . . .)[264**].

α-$NaClO_4$ [265, 266*]; α-$(NH_4)ClO_4$ [265]; β-(cubic)-$RClO_4$ (R = Na, Ag, NH_4, K, Rb, Cs, Tl) [267*, 268*].

$AgMnO_4$ [270*]; $SrCrO_4$ [271]; $PbCrO_4$ [272]; KBF_4 [274]; Na_2SO_4 [277*]; polymorphs of Na_2SO_4 [275]; Ag_2SO_4 [276*]; K_2SO_4 [278*]; K_2CrO_4 [279*, 280**]; $(NH_4)_2CrO_4$ [281*]; $Ca_5F(PO_4)_3$ (apatite) [283**, 284*]; $AgHgI_4$ [285*]; KPF_6, NH_4PF_6, $CsPF_6$ [286]; Na_3AlF_6 [287*]; $(NH_4)_3AlF_6$ [288*, 289*]; $K_2Cr_2O_7$, $(NH_4)_2Cr_2O_7$ [290*, 291]; $K_2S_2O_6$ [292**, 293*].

Group : $CaCrO_4$ (crocoite), CaI_2O_6 (lautarite), CaI_2O_6,$CaCrO_4$ (dietzite) [294*].

Systems : $HgSO_4$–$HgCl_2$, $HgSO_2$–HgI_2.[295] Reactions between solid salts.[296]

7. *Salt hydrates, co-ordination compounds, etc.*

Known type : *H41.* $(NH_4)_2CuCl_4,2H_2O$.[301]

New structures : $CuSO_4,5H_2O$ (dehydration of) [297]; $CaSO_4,2H_2O$ (gypsum)[298**], $CaHPO_4,2H_2O$ (brushite), $Ca_2SO_4,CaHPO_4,4H_2O$ (ardealite) [299*]; $BeSO_4,4H_2O$ [300**]; $M^{II}X_2(H_2O)_6$ (M = Ca, Sr, Ba; X = Cl, Br, I) [302]; $M^{II}M^{IV}X_6^{-I}(H_2O)_6$ (M^{II} = Mg, Mn, Fe, Ni, Co, Zn; M^{IV} = Si, Ti, Zr, Sn, Pt; X = F, Cl, Br, I), $M^{II}M^{III}(CN)_6(NH_3,H_2O)_6$ (M^{II} = Co . . .; M^{III} = Cr, Fe, Co . . .) [304**]; $M_2^IM^{II}(XO_4)_2,6H_2O$ (M^I = K, NH_4, Tl, etc.; M^{II} = Mg, Fe, Zn, Cd, etc.; X = S, Se, etc.) [305*, 306**]; $K_3M^{III}(CN)_6$ (M^{III} = Cr, Mn, Fe, Ir) [307*]; $K_2PbM^{II}(NO_2)_6$, $K_3Mn(NO_2)_6,3H_2O$(M = Cu, Ni . . .) [308]; $NaUO_2(CH_3{\cdot}CO{\cdot}O)_3$ [309]; $(H{\cdot}COO)_2Cu,2H_2O$ and $4H_2O$ [310, 311]; $C(NH_2)_3Cl$ [312*]; $(SMe_3)_2SnCl_6$, $(SMe_2Et)_2SnCl_6$, $(PMeEt_3)_2SnCl_6$.[313*]

8. *Complex oxides and hydroxides.*

Spinel type : *H11.* General [325, 326, 327]; $MgAl_2O_4$ [329**]; $MgFe_2O_4$, $MgGa_2O_4$[330**]; $ZnFeO_4$, $CdFe_2O_4$ [333]; $MgCr_2O_4$, $CdCr_2O_4$ [334]; $CuAl_2O_4$, $ZnAl_2O_4$, $ZnCr_2O_4$, $ZnFe_2O_4$, $MnFe_2O_4$ [335]; $ZnGa_2O_4$ [331]; Co_2TiO_4, Zn_2TiO_4 [336]; Mg_2TiO_4, Co_2TiO_4, Zn_2TiO_4, Mn_2TiO_4 [337]; Ni_2GeO_4 [338]; Zn_2TiO_4, Zn_2SnO_4 [339].

γ-Alumina type : γ-Al_2O_3 [324]; Fe_2O_3 (magnetic) [328**].

Hausmannite type : $CdIn_2O_4$, $CaIn_2O_4$.[340*]

Related structure : $Na_2Al_{23}O_{35}$ (β-alumina) [345**]; $Ca_3Al_2O_6$ [346*]; $CaFe_2O_4$,$CdFe_2O_4$,(Sr,Ba,Pb)Fe_2O_4.[325]

Ilmenite type : *G4.* $NiTiO_3$ [339]; $FeTiO_3$.[343]

Related structures : (Fe,Mn)$(Nb,Ta)_2O_6$ (columbite) [341**]; Fe_2TiO_5 (pseudobrookite).[342**]

Perovskite type : *G5.* $(Ca,Ce,Na)_2(Nb,Ti)_2O_6$ (loparite).[349*]

Pyrochlor type : $(Na,Ca)_2Nb_2O_6(O,OH,F)$ (pyrochlorite) [349*]; $(Ca,Mn,Na_2)_2Sb_2O_7$ (atopite and mauzelite) [356*]; $(Ca,Ce,La,K)_2(Nb,Fe)_2O_6(O,OH,F)$ (koppite).[357*]

Garnet type : *H31.* $NaCa_2Mn_2As_3O_{12}$ (berzeliite) [358*] ; $Na_3Li_3Al_2F_{12}$ (cryolithionite).[359*]

Complex hydroxides : AlO(OH),FeO(OH),MnO(OH) [319, 320, 321] ; $Fe_2O_3,4H_2O$[322] ; $Be_2BO_3(OH)$ (hambergite) [344**] ; K, $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Al(SO_4)(OH),H_2O$ (voltaite and similar compounds) [352, 353] ; $x PbCl_2$, $y AgCl$, $z Cu(OH)_2$ (boleite, pseudoboleite, cumengite) [348] ; $Mn_3(AsO_4)_2,2Mn(OH)_2$ (arsenoclasite).[355]

Systems : $Ba(OH)_2$–H_2O, NiO–Ni_2O_3–H_2O, FeO–Fe_2O_3–H_2O [314] ; Al_2O_3–H_2O [315–318] ; V_2O_5–H_2O, Nb_2O_5–H_2O, Ta_2O_5–H_2O [323] ; $MgCO_3$–$Mg(OH)_2$–H_2O [351] ; $Zn(OH)_2$–ZnX_2–H_2O (X = Cl, Br, I, NO_3, $\frac{1}{2}SO_4$) [350] ; MgO–FeO–Fe_2O_3[332] ; $CaAl_2O_4$–H_2O [347] ; Fe_2O_3–CuO–SO_3–H_2O.[354]

9. *Silicates.*

General [360, 361] ; germanates [338].

Orthosilicate types : Ni_2SiO_4, olivine type [339] ; $Bi_4(SiO_4)_3$ (eulytite) [362**] ; $CaTiSiO_5$ (titanite) [363**] ; Al_2SiO_5 (cyanite, sillimanite, andalusite) (revision) [365**] ; Mn_7SiO_{12} (braunite).[364]

Polysilicate types : $Sc_2Si_2O_7$ (thortveitite) [366**] ; $(Ca,Na)_2(Mg,Al)(Si,Al)_2O_7$ (melitite) [367**] ; $Ca_2ZnSi_2O_7$ (hardystonite) [368*] ; $(Ca,Na)_2Be(Si,Al)_2(O,OH,F)_7$ (meliphanite) [369*] ; $Ca_{10}Al_4(Mg,Fe)_2Si_9O_{34}(OH)_4$ (vesuvianite) [370**] ; $H_xXY_9B_3Si_6O_{31}$ (tourmaline) [371, 372] ; $BaTiSi_3O_9$ (benitoite) [373**] ; $(Na,Ca,Fe)_6ZrSi_6O_{18}(OH,Cl)$ (eudialite).[374]

Metasilicate types : $CaSiO_3$ (wollastonite), $HNaCa_2(SiO_3)_3$ (pectolite).[375*, 376*]

Monoclinic pyroxenes : $XY(SiO_3)_2$ (diopside) (X = Ca, Na ; Y = Mg, Fe^{III}, Al) [376**] ; $XY(SiO_3)_2$ (clino-enstatite) (X = Li, Mg ; Y = Mg, Al).[376**]

Rhombic pyroxenes : $(Mg,Fe)(SiO_3)_2$ (enstatite).[377**, 378*]

Monoclinic amphiboles : $H_2Ca_2Mg_5(SiO_3)_8$ (tremolite).[379**]

Rhombic amphiboles : $H_2Mg_7(SiO_3)_8$ (anthophyllite) [380**] ; other amphiboles.[381–383*]

Serpentine : $H_4Mg_3Si_2O_9$ (chrysolite).[384**]

Mica types : Micas ; $KX_nY_4O_{10}(OH,F)_2$ (X = Mg, Fe^{II}, Fe^{III}, Mn^{II}, Mn^{III}, Ti, Li ; Y = Si, Al ; n = 2—3) ; $CaX_nY_4O_{10}(OH,F)_2$ (brittle micas) [385*] ; $KAl_2(Si_3Al)O_{10}(OH)_2$ (muscovite).[386**]

Chlorites : $X_nY_4O_{10}(OH)_8$ [387*] (kaolins) ; $Al_2Si_2O_{10}(OH)_8$ [388–391] ; $H_8KCa_4Si_8O_{20}(OH)_8F$ (apophyllite) [392**] ; Be_2SiO_4 (phenakite), Zn_2SiO_4 (willemite) [393**] ; $(MnFe_4)Si_3O_7(OH,Cl)_6$ (pyrosmalite) [394] ; $AlBeSiO_4(OH)$ (euclase), $CaBSiO_4(OH)$ (datolite) [395*] ; $Al_2(Al,Fe)Ca_2(SiO_4)_3(OH)$ (epidote).[396–398*]

Felspar types: $CaB_2Si_2O_8$ (danburite)[399**]; (Ca, Na, K) $(Si,Al)_4O_8$ (felspars).[400*]

Nepheline type: $X_2Y_2Si_2O_8$ (X = Li, Na, K; Y = Al, Sc, Y, La, Nd, Pr, Sm, Er)[401, 402*]; $NaAlSiO_4$ (nepheline)[403*, 404*]; $KAlSiO_4$ (kaliophilite)[404*, 405*]; $NaAlSi_2O_6,H_2O$ (analcite)[403, 406**, 407**, 408*, 409]; $LiAlSi_4O_{10}$ (petalite).[410*]

Zeolites[411]; $Na_4Al_3Si_3O_{12}Cl$ (sodalite), $(Mn,Fe,Zn)_4Be_3Si_3O_{12}S$ (helvine)[412*]; $Na_2Al_2Si_3O_{10},2H_2O$ (natrolite)[411*, 413*, 414];

$(Na,Ca)_4Al_3(Al,Si)_3Si_6O_{24}(Cl,SO_4,CO_3)$

(scapolite)[411*,416]; $(Na,Ca)_4Al_3Si_3O_{12}(CO_3,SO_4,Cl)$ (davyne)[411*, 417]; (cancrinite)[411*, 417, 418]; $(Na,Ca)Al_2Si_7O_{18},6H_2O$ (heulandite)[414, 415*]; $CaAl_2Si_4O_{12},6H_2O$ (chabazite)[419*, 420]; other hydrous silicates: chamosite,[421] pyrosmalite.[422*]

Silicate systems and synthetic silicates: Fe_2O_3–SiO_2[425]; Cr_2O_3–SiO_2[423]; MgO–SiO_2[425]; K_2O–CaO–SiO_2[424]; CaO–SiO_2–H_2O[431]; β-$CaSiO_3$[428]; γ-Ca_2SiO_4, Ca_3SiO_5, $Ca_3Al_2O_6$[429]; Ca_2SiO_4[430]; glasses.[432, 433]

10. *Simple molecular compounds.*

Known types: *A1.* Ne[435]; Kr[436, 437]; Xe[438]; HCl, HBr (high)[440]. *A3.* H_2 (para).[439]
C2. CO_2, N_2O.[446] *C10.* H_2O.[458, 459]
D1. PH_3, AsH_3.[443] *D11.* SiI_4[451]; $ZrCl_4$.[452*]
O1. CH_4.[448, 449**] *O11.* CHI_3.[449a]

New structures: HCl, HBr, HI (low)[440]; H_2S, H_2Se[441*, 442]; NO_2[444*, 445]; COS[447*]; SiF_4[450**]; UCl_4[452]; $Fe_3(CO)_{12}$[455*]; $B_{10}H_{14}$[456]; $C(CH_2{\cdot}O{\cdot}CHO)_4$, pentaerythritol tetraformate[453, 454*]; $Si(OCH_3)_4$[457**]; S, Se[460, 461*, 462, 463]; P[464, 465]; Sb (explosive).[466]

Organic.—General.[468]

11. *Long-chain compounds.*

Paraffins[469, 470**, 471, 472, 474–476]; $C_{34}H_{70}$ (2-dimensional crystals[473]; *n*-fatty acids[477, 478, 479, 480, 481]; dicarboxylic acids[482*]; alcohols[483]; $C_nH_{2n+1}NH_3I$ (n = 4–12)[485**, 486**, 489**] (rotation).

Unsaturated chains: $CHBr_2{\cdot}CBr{:}CBr{\cdot}CHBr_2$[484*];

$CH_3{\cdot}O{\cdot}CO[{\cdot}CH{:}CH{\cdot}C(CH_3){:}CH{\cdot}]_nCH{:}CH{\cdot}CO{\cdot}OCH_3$,

methyl bixin[487*]; $C_6H_5{\cdot}[CH{:}CH]_n{\cdot}C_6H_5$, diphenylpolyenes[488**].

12. *Other aliphatic compounds.*

Amino-compounds: $(NH_2)_2CO$, urea[490**]; $NH_2{\cdot}CH_2{\cdot}CO_2H$, glycine[491**, 492*]; amino-acids[492*]; peptides[492*, 493]; diketopiperazine[492*]; diethylbarbituric acid[494*]; *d* + *dl-spiro*-hydantoin.[495*]

Sugars : *d*-glucose [496*, 497*]; *d*-lævulose [496*]; mannitol, dulcitol, mannose [498, 499*, 500*]; arabinose, xylose, rhamnose [501*, 502*]; lactones and pyranoses.[503*]

cyclo-Hexane derivatives: *cyclo*hexene, *trans*-dibromo*cyclo*hexane [504, 505*]; quebrachitol, inositol, quercitol [504*, 505*, 506*]; *cyclo*hexanediols.[506*, 507*]

13. *Aromatic compounds.*

Benzene, thiophen [508]; hexachlorobenzene [509***]; hexa-aminobenzene [510]; 1 : 3 : 5-trinitrobenzene, 2 : 4 : 6-trinitrotoluene [527]; picric acid [511]; trinitroresorcinol, trinitrophloroglucinol [512*]; lead styphnate [246*]; *o*-, *m*-, and *p*-dinitrobenzene, 4 : 6-dinitroxylene, 2 : 6-dinitrophenol [513*]; 2 : 4 : 6-tribromobenzonitrile [514*]; *m*-iodobenzoic acid [515**]; naphthalene and anthracene [516**, 517**, 518]; anthraquinone [519*]; azobenzene [520]; *p*-nitrostilbene [521*]; diphenyl, dimesityl, *dl*-3 : 3′-diaminodimesityl, hexachlorodiphenyl, diphenic acid, *o*-tolidine [522, 523]; naphthacarbazole [531*]; aniline picrate, 2 : 4 : 6-trinitrodiphenylamine [529*]; tetrabromo-α- and -β-naphthylamine [530]; triphenylbismuthine dichloride [525*]; strychnine [532*]; harmine [533*]; graphite and graphitic acid [523, 524]; other complex organic compounds [531, 534]; molecular compounds,[519*, 526*, 527*, 528*, 530*]

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[490] *Ibid.*, 1930, **75**, 529; *A.*, 550. [491] *Ibid.*, 1931, **77**, 424; *A.*, 790. [492] *Ibid.*, 1931, **78**, 363; *A.*, 1002. [493] F. V. Lenel, *Naturwiss.*, 1931, **19**, 19; *A.*, 152. [494] E. Hertel, *Z. physikal. Chem.*, 1930, [*B*], **11**, 279; *A.*, 289. [495] (Sir) W. Pope and J. B. Whitworth, *Proc. Roy. Soc.*, 1931, [*A*], **136**, 357. [496] *Z. Krist.*, 1929, **72**, 301; *A.*, 1930, 983. [497] O. L. Sponsler and W. H. Dore, *J. Amer. Chem. Soc.*, 1931, **53**, 1639; *A.*, 790. [498] *Nature*, 1931, **127**, 11; *A.*, 152. [499] T. C. Marwick, *Proc. Roy. Soc.*, 1931, [*A*], **131**, 621; *A.*, 897.

[500] G. W. McCrea, *Nature*, 1931, **127**, 162; *A.*, 290. [501] *Z. Krist.*, 1931, **78**, 477; *A.*, 1116. [502] *J.*, 1931, 2313; *A.*, 1275. [503] J. Young and F. W. Spiers, *Z. Krist.*, 1931, **78**, 101; *A.*, 1219. [504] *Z. Elektrochem.*, 1931, **37**, 540; *A.*, 1219. [505] *Tidsskr. Kjemi Berg.*, 1930, **10**, 128; *A.*, 27. [506] *Z. Krist.* 1931, **78**, 76; **80**, 1; *A.*, 1219. [507] *Ibid.*, 1931, **80**, 5; *A.*, 1219. [508] G. Bruni, and G. Natta, *Atti R. Accad. Lincei*, 1930, [vi], **11**, 929, 1058; *A.*, 152. [509] *Proc. Roy. Soc.*, 1931, [*A*], **133**, 536.

[510] *Ibid.*, 1931, [*A*], **131**, 612; *A.*, 897. [511] M. A. Bredig and H. Möller, *Z. Krist.*, 1929, **71**, 331; *A.*, 1930, 672. [512] *Z. physikal. Chem.*, 1931, [*B*], **12**, 139; *A.*, 551. [513] E. Hertel, *ibid.*, 1930, [*B*], **7**, 188; *A.*, 1930, 668. [514] M. A. Bredig, *Z. Krist.*, 1930, **74**, 56; *A.*, 672. [515] H. P. Klug, E. Mack, jun., and F. C. Blake, *J. Amer. Chem. Soc.*, 1929, **51**, 2880; *A.*, 1929, 1368. [516] J. M. Robertson, *Proc. Roy. Soc.*, 1929, [*A*], **125**, 542; *A.*, 1929, 1367. [517] *Nature*, 1930, **125**, 456; *A.*, 1930, 528. [518] *Ibid.*, p. 456; *A.*, 1930, 528. [519] E. Hertel and G. H. Römer, *Z. physikal. Chem.*, 1930, [*B*], **11**, 90; *A.*, 152.

[520] M. Prasad, *Phil. Mag.*, 1930, [vii], **10**, 306; *A.*, 1930, 1241. [521] E. Hertel and G. H. Römer, *Z. Krist.*, 1931, **76**, 467; *A.*, 550. [522] G. L. Clark and L. W. Pickett, *Proc. Nat. Acad. Sci.*, 1930, **16**, 20; *A.*, 1930, 528; *J. Amer. Chem. Soc.*, 1931, **53**, 167; *A.*, 290. [523] H. Thiele, *Kolloid-Z.*, 1931, **56**, 129; *A.*, 1124; *Z. anorg. Chem.*, 1930, **190**, 145; *A.*, 1930, 872. [524] *Ber.*, 1930, **63**, [*B*], 1248; *A.*, 1930, 875; *Z. Elektrochem.*, 1931, **37**, 613. [525] G. Greenwood, *Amer. Min.*, 1931, **16**, 473. [526] E. Hertel and H. Kleu, *Z. physikal. Chem.*, 1930, [*B*], **11**, 59; *A.*, 153. [527] E. Hertel and G. H. Römer

ibid., p. 77; *A.*, 153. [528] E. Hertel, *ibid.*, Bodenstein Festband, 1931, 267; *A.*, 1219. [529] E. Hertel and K. Schneider, *ibid.*, 1931, [*B*], **12**, 109; *A.*, 415. [530] *Idem, ibid.*, 1931, [*B*], **13**, 387; *A.*, 1114; *Z. Elektrochem.*, 1931, **37**, 536; *A.*, 1218. [531] A. Ferrari and A. Scherillo, *Z. Krist.*, 1931, **80**, 45; *A.*, 1219. [532] T. C. Marwick, *Nature*, 1930, **126**, 438; *A.*, 1930, 1353. [533] *Z. Krist.*, 1930, **74**, 202. [534] A. Burgeni, F. Halla, and O. Kratky, *ibid.*, 1929, **71**, 263; *A.*, 1930, 844.

J. D. BERNAL.
W. A. WOOSTER.

COLLOID CHEMISTRY.

I WAS entrusted by the Council to arrange for the preparation of a Report on Colloid Chemistry. The last Report (1925) consisted largely of a general summary of the whole subject. Since it has been found by experience that in such special fields a Report reviewing some selected topics of importance is of more general utility than one covering the whole range of subjects, I have asked Dr. W. T. Astbury, Mr. D. C. Henry, and Dr. R. K. Schofield to prepare monographs on branches of colloid chemistry with which they are particularly well acquainted.

E. K. RIDEAL.

PART I.—THE STRUCTURE OF FIBRES.

By W. T. ASTBURY.

The very considerable advances in our knowledge of the structure of fibres that have been made during the last five years or so are due almost entirely to the interpretation of their *X*-ray diffraction photographs in the light of developments in the chemistry of compounds of high molecular weight. For a number of years previously [1] it had been known that vegetable and animal fibres give rise to characteristic *X*-ray photographs—now generally described as "*X*-ray fibre photographs"—but for reasons which appear below, these photographs were of too indeterminate a nature to be analysed successfully without the help of more decisive chemical information than was at the time available. The deduction, by Haworth, Freudenberg, and others,[2] of the structural formula of cellulose as a long chain of hexagonal ring systems proved sufficient, however, to supply the chemical impulse required, and from that time onwards the subject has developed so rapidly, the *X*-ray and chemical results mutually reinforcing one another, that it is now possible to form a comprehensive picture of the whole field of fibre structure and refer each individual case to comparatively simple common principles.

[1] P. Scherrer, *Nach. Ges. Wiss. Göttingen*, 1918, 98; R. O. Herzog and W. Jancke, *Z. Physik*, 1920, **3**, 196; R. O. Herzog, W. Jancke, and M. Polanyi, *ibid.*, p. 343; M. Polanyi, *Naturwiss.*, 1921, **9**, 337; O. L. Sponsler, *J. Gen. Physiol.*, 1925–26, **9**, 221, 677; O. L. Sponsler and W. H. Dore, *Colloid Symposium Monograph*, 1926, **4**, 174; O. L. Sponsler, *Nature*, 1927, **120**, 767; 1930, **125**, 633; *Naturwiss.*, 1928, **16**, 263.

[2] W. N. Haworth, "The Constitution of Sugars," London, 1929.

PLATE I.

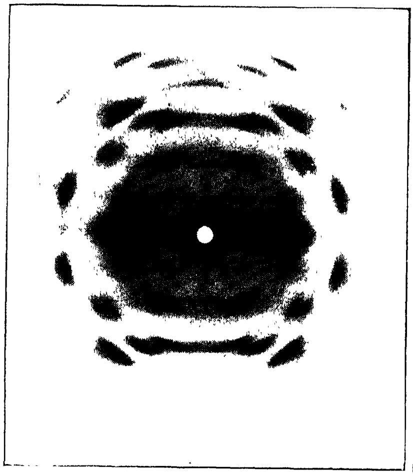


FIG. 1.—RAMIE.

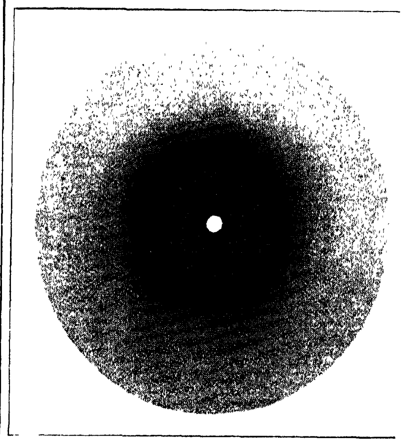


FIG. 2.—UNSTRETCHED RUBBER.

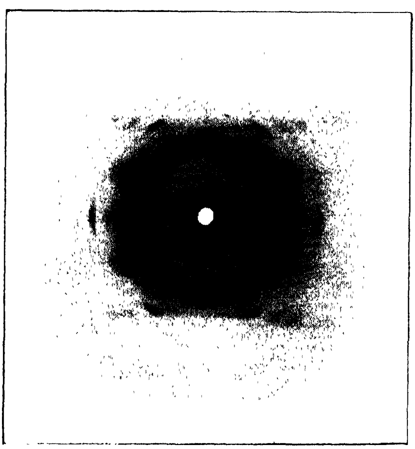


FIG. 3.—STRETCHED RUBBER.

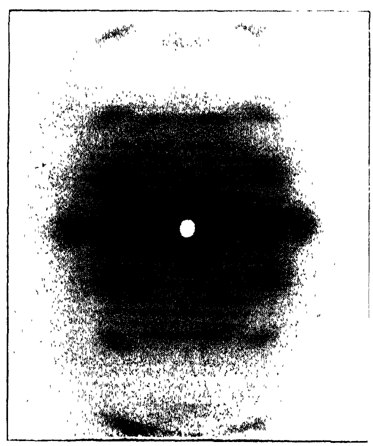


FIG. 4.—NATURAL SILK.

[*To face page* 322.

PLATE II.

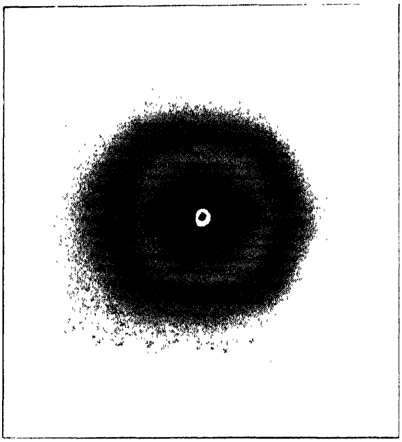


FIG. 5.—α-KERATIN.

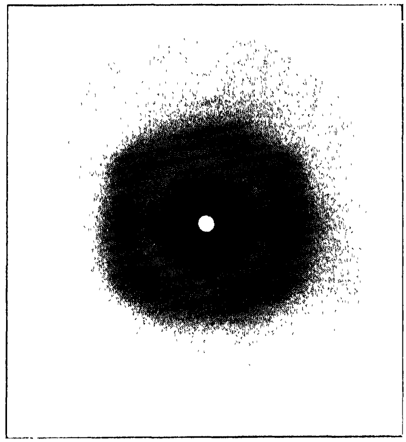


FIG. 6.—β-KERATIN.

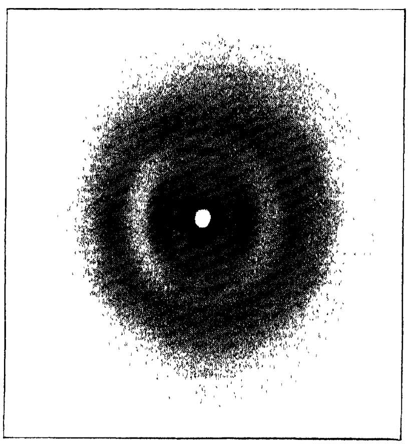


FIG. 7.—FEATHER KERATIN.

A very thorough and valuable account of the structure of compounds of high molecular weight, in both their chemical and their crystallographic aspects, was given by K. H. Meyer and H. Mark in 1930,[3] and more recently the scheme has been completed by the inclusion of the elastic protein fibres such as hair.[4]

General Characteristics.

A typical *X*-ray fibre photograph, obtained simply by sending a fine beam of *X*-rays perpendicularly through a bundle, about 1 mm. thick, of parallel fibres, is that of ramie (Plate I, Fig. 1). This substance gives one of the best-defined fibre photographs known, in the sense that it simulates closely the ideal " rotation photograph " of a single visible crystal; but it has, in common with the more indeterminate photographs of silk, hair, etc., certain features which we have learnt always to associate with the structure of natural fibres. In the first place, the ideal fibre photograph is geometrically equivalent to the single crystal rotation photograph, that is, the photograph given by a single crystal rotating about an axis perpendicular to the *X*-ray beam. It follows from this that fibres are in general composed, either wholly or partly, of a multitude of crystals, or pseudo-crystals, so lying in the body of the fibre as to have always one and the same crystallographic axis approximately parallel to the length of the fibre, while all crystallographic directions perpendicular to this preferred axis are in random orientation.* In the second place, the crystalline particles of the fibre substance, whose existence is thus demonstrated by *X*-ray reflexion even though their dimensions are submicroscopic, must be considerably longer than they are thick, because the *X*-ray reflexions, or " spots," lying on or near the equator of the typical fibre photograph are always broader and more diffuse than those lying on or near the meridian of the photograph. This is a consequence of the diffraction principle, according to which the resolving power decreases with the number of diffracting centres. The fibre crystals are therefore long enough in a direction parallel to the fibre axis to contain sufficient diffracting centres to give rise, on the meridian, to comparatively sharp spots (which are *X*-ray reflexions, from planes perpendicular to the fibre length), but so thin perpendicular to the fibre axis that the crystal planes parallel to this axis reflect only broad, diffuse

[3] " Der Aufbau der hochpolymeren organischen Naturstoffe," Leipzig, 1930.

[4] W. T. Astbury, " The Molecular Structure of Natural Fibres." (A lecture published by Metropolitan-Vickers Electrical Co., Manchester, 1931.)

* Such an effect could arise, of course, simply from the fact of using a *bundle* of fibres for the *X*-ray photograph, but the present evidence is that there is no selective orientation perpendicular to the fibre, even in single fibres (see later).

X-ray beams. In general, we may say that the crystallites have an average thickness of no more than 100 Å.U., and an average length perhaps ten times as great (see below).

It is natural to identify these long, thin crystallites revealed by X-rays with the " micelles " postulated long ago by C. Nägeli [5] and investigated in detail more recently with the aid of polarised light,[6] since water adsorption in cellulose, silk, wool, etc., produces a percentage lateral swelling which is some 15 times greater than the longitudinal swelling without a corresponding change occurring in the X-ray photographs. The water is therefore in the main adsorbed on the surface of the crystallites or micelles. It does not follow, of course, that we are justified in ascribing sharp boundaries to the crystallites : the observed X-ray and swelling effects could quite well arise from ill-defined aggregates of widely varying thickness.

The combination of numerous X-ray observations with the most recent concepts in the chemistry of compounds of high molecular weight leads to the conclusion that the elongated, submicroscopic crystallites which are the basis of fibre structure are in reality no other than bundles, of various thicknesses and of varying degrees of perfection, of long-chain molecules which are in general linear polymerides of relatively simple chemical units. For instance, cellulose molecules being long chains of β-glucose residues linked by primary valencies—what are known in German literature as " Hauptvalenzketten "—it is clear that such chains can be grouped together by the operation of ordinary crystallographic forces to form bundles, long and of well-defined periodicity parallel to the fibre axis, but thin and possibly of ill-defined periodicity perpendicular to the fibre axis.

Reversible Transformations in Fibre Structure.

The X-ray photographs of natural silk (fibroin), and of the various cellulose fibres, both natural and artificial, exhibit no fundamental change when the fibres are stretched even to the breaking point. In those cases where there is a lack of strict alinement of the crystallites, the alinement is improved by stretching, as might be expected ; but the essential features of the photographs remain unchanged. On the other hand, the photograph of animal hairs (keratin) undergoes, at extensions exceeding about 25%, a transformation into another, and different, fibre photograph, which is replaced once more by the normal photograph when the fibres are returned to their original length.[7] The two X-ray photographs of hair are thus a physical

[5] " Die Micellartheorie " (Ostwald's Klassiker der exakten Wissenschaften, Nr. 227, Leipzig, 1928) ; H. Mark, *Naturwiss.*, 1928, **16**, 892.

[6] A. Frey, *Jahrb. wiss. Bot.*, 1925–26, **65**, 195 ; A. Frey-Wyssling, *Z. wiss. Mikr.*, 1930, **47**, 1.

[7] W. T. Astbury, *J. Soc. Chem. Ind.*, 1930, **49**, 441 ; *J. Text. Sci.*, 1931, **4**, 1.

record of a reversible intramolecular transformation involving change of length. That rubber undergoes an intramolecular transformation on stretching was discovered by J. R. Katz,[8] but in this case the change is from an amorphous state (unstretched) to a crystalline state (stretched). Except for this difference, that the *X*-ray photograph of normal rubber (Plate I, Fig. 2) is an " amorphous photograph " and that of stretched rubber (Plate I, Fig. 3) a true fibre photograph, while the photographs of both normal and stretched hair are fibre photographs, the two reversible changes appear to be quite analogous, and due to the unfolding of coiled molecular chains which tend to return to their original folded state when the tension is removed. It seems clear that the molecular chains of rubber are polymerised isoprene, while those of keratin are apparently polypeptides.

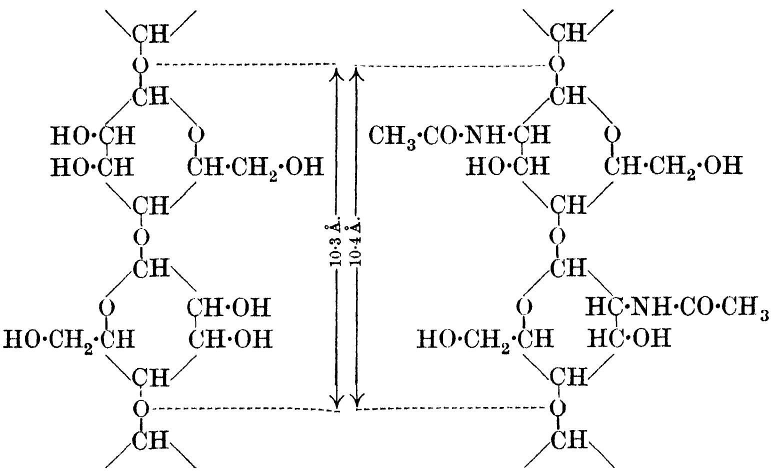
The General Theory of Fibre Structure.

The special features of natural fibres revealed by *X*-ray analysis and described briefly above suffice to give a rational explanation of their general properties in comparatively simple terms.[3, 4] It has already been mentioned how the well-known swelling and optical phenomena follow, but perhaps the most striking conclusions relate to their characteristic elastic properties. Natural silk and the cellulose fibres exhibit only a little true elasticity, since Hooke's law fails at extensions of 1 or 2%, and there is only a partial recovery from higher extensions. (This partial recovery is the so-called " Nachwirkung," and is probably due to irregularities among the micelles and on their surfaces.) If now the molecular chains which are the basis of fibroin and cellulose are already extended as far as is stereochemically permissible, fibres built from them in the way described will stretch only in virtue of internal slipping between the chain bundles, and complete recovery from extension beyond the Hooke's law limit will be impossible. This argument is in full agreement with the findings of *X*-ray analysis, which show (1) that the repetition of chemical pattern along the fibre axis corresponds closely with what we should expect from extended polypeptide and cellulose chains, respectively (see Fig. 2 and Fig. 1*a*); and (2) that the chain bundles are preserved more or less intact during extension. It seems probable that the fibres break finally through a complete separation of micelles at the point of rupture, for Meyer and Mark [3] have shown that the work required to break a cellulose fibre is less than what would be required to break the primary valency bonds in the molecular chains. Nevertheless, owing to the great length of these chains and the additivity of intermolecular forces along their

[8] *Chem.-Ztg.*, 1925, **49**, 353; *Naturwiss.*, 1925, **13**, 411.

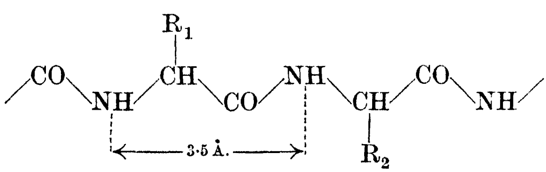
sides, the strength of natural fibres is still comparable with that of metal wires of the same thickness.

Fig. 1a. Fig. 1b.



Cellulose chain. Chitin chain.

Fig. 2.



This line of reasoning obviously fails—or, at least, is incomplete—in the case of animal hairs, simply because the photograph of unstretched hair does *not* agree with what we should expect from extended peptide chains such as we must conclude are present in natural silk. Similarly, the photograph of unstretched rubber is also anomalous, for it is only an " amorphous " photograph containing no information at all as to periodicities in the chains of polymerised isoprene. But the *X*-ray analyses of both *stretched* hair and *stretched* rubber are in good accord with previous chemical considerations, for we find that the photograph of stretched hair is analogous to that of unstretched silk,[9] while that of stretched rubber can be explained on the basis of long molecular chains with periodicity corresponding to isoprene units linked in the *cis*-configuration.[10]

[9] W. T. Astbury and A. Street, *Phil. Trans.*, 1931, [*A*], **230**, 75; W. T. Astbury and H. J. Woods, *Nature*, 1930, **126**, 913.

[10] K. H. Meyer and H. Mark, *Ber.*, 1928, **61**, 1939; H. Fikentscher and H. Mark, *Kolloid-Z.*, 1929, **49**, 135.

Stretched hair, then, is built of fully extended peptide chains like those in natural silk (whether stretched or unstretched), and stretched rubber is built of extended isoprene chains which form crystallites on alinement. Both substances, when the tension is released, may be caused to recover their original length—in the case of hair, through the action of water, etc.,[11] and in the case of rubber through the action of heat [12]—whereupon the original (abnormal) photographs reappear. The remarkable long-range elasticity of hair and rubber—hair may be stretched to twice,[9] and rubber to ten times its original length [13]—is thus, in each case, to be ascribed simply to an intramolecular change which may be brought about by tension, and is accompanied by unfolding of molecular chains and consequent considerable elongation. As would be expected, the load-extension curves of hair and rubber are closely analogous,[4] just as are those of viscose and natural silk.[4]

The main fundamental properties of natural fibres may therefore be explained in terms of the following three generalisations :

(1) Fibres are built of long, thin, sub-microscopic crystallites or micelles, which are bundles, of various sizes and of various degrees of perfection, of molecular chains of relatively simple chemical units linked before and behind by primary valencies. In cases such as silk, ramie, hair, wool, etc., the crystallites lie with their long axes roughly parallel to the fibre axis; in other cases, such as cotton, they are inclined at a constant angle to the fibre axis.[14] The optical properties, adsorption phenomena,[15] and the general physico-chemical behaviour [3] of fibres are the consequences of this sub-crystalline or micellar structure.

(2) Fibres may consist of extended molecular chains, *e.g.*, cellulose, natural silk, stretched rubber, stretched hair, or of folded molecular chains, *e.g.*, unstretched rubber and unstretched hair.

(3) The extended molecular chains being incapable of further extension, fibres composed of such chains extend by internal slipping from which they cannot recover their original length : but folded chains may unfold and pass into the extended state, thus giving rise to long-range elasticity. An intermediate form of extension phenomenon is that due to alinement of chains or micelles : the maximum possible extension by this mechanism is 57%.[16]

[11] S. Shorter, *J. Text. Inst.*, 1924, **15**, 207T; *J. Soc. Dyers Col.*, 1925, **41**, 212; J. B. Speakman, *J. Text. Inst.*, 1926, **17**, 457T; 1927, **18**, 431T.

[12] L. Hock, *Kolloid-Z.*, 1925, **35**, 40.

[13] H. Mark and G. von Susich, *ibid.*, 1928, **46**, 11; *A.*, 1928, 1186.

[14] R. O. Herzog and W. Jancke, *Z. physikal. Chem.*, 1928, [*A*], **139**, 235.

[15] J. B. Speakman, *J. Soc. Chem. Ind.*, 1930, **49**, 209T.

[16] H. J. Poole, *Trans. Faraday Soc.*, 1925, **21**, 114; *A.*, 1925, ii, 519; W. T. Astbury and A. Street, *Phil. Trans.*, 1931, *A*, **230**, 75.

Cellulose and its Derivatives.

During the last few years a considerable amount of information has been acquired, chiefly by *X*-ray analytical methods, concerning the detailed molecular structure of the two forms of cellulose, native cellulose and mercerised cellulose ("Hydratcellulose"), and of sixteen of their derivatives. It is impossible here to go into these results with any thoroughness, but K. Hess and C. Trogus [17] have compiled a valuable summary in which it is shown how the two celluloses and ten of their derivatives appear to be based on a periodicity along the fibre axis of 2 × 5·15 Å.U., while of the remaining six derivatives, in order to interpret their *X*-ray photographs, it seems necessary to assume for four of them 3 × 5·15 Å.U., for another 4 × 5·15 Å.U., and for still another (trinitrocellulose) 5 × 5·15 Å.U. It is concluded from these data that the dimension, 5·15 Å.U., which is the length of a glucose residue, stands in a closer relation to the constitution of cellulose than does the dimension, 10·3 Å.U., the length of a cellobiose residue (see Fig. 1*a*); that is to say, that the cellobiose residue does not pre-exist in the cellulose molecule, as has been suggested by Haworth.[2] It is true that these anomalous fibre periodicities are at the moment a source of some disquiet with regard to the true nature of the cellulose chain, but in view of the fact that many existing fibre photographs defy unambiguous evaluation, there does not yet appear to be sufficient reason to accept the conclusions of Hess and Trogus as final. The *cellulose* chain may be based fundamentally on a repetition of the cellobiose residue, but it does not follow from this that the periodicity of the chain should remain a constant multiple of 5·15 Å.U. for each and every possible type of addition or substitution reaction along its sides. Moreover, it is only in the case of native cellulose [18] and of mercerised cellulose [19] that we can feel any certainty about the true size of the unit of pattern.

The atomic arrangement in the two celluloses has now been investigated in some detail; but it will suffice here to state that they bear a very simple relation to each other based on a small rotation of the molecular chains about their long axes.[20] It would appear that mercerised cellulose is the stable form, since it is always produced from the native fibre when the latter has been sufficiently

[17] *Z. physikal. Chem.*, Bodenstein Festband, 1931, 385.

[18] H. Mark and K. H. Meyer, *ibid.*, 1929, [*B*], **2**, 115; R. K. Andress, *ibid.*, p. 380; O. L. Sponsler, *Nature*, 1930, **125**, 633; *Protoplasma*, 1931, **12**, 241; R. O. Herzog and W. Jancke, *Z. physikal. Chem.*, 1928, [*A*], **139**, 235.

[19] R. K. Andress, *ibid.*, 1929, [*B*], **4**, 190; A. Burgeni and O. Kratky, *ibid.*, p. 401; K. Weissenberg, *Naturwiss.*, 1929, **17**, 181.

[20] W. T. Astbury and T. C. Marwick, *Nature*, 1931, **127**, 12.

swollen to separate the chains, and the swelling agent afterwards removed. Much of our knowledge of the structure of the cellulose derivatives is due to a long series of investigations by Hess and Trogus.[21] As would be expected, the side spacings of the crystallites formed in these derivatives vary in a manner depending on the nature of the groups substituted down the sides of the original cellulose chains, while, as mentioned above, in the majority of cases investigated the fibre period remains unaltered (10·3 Å.U.). The chitin chain, an acetylglucosamine chain, is shown diagrammatically in Fig. 1*b*. Its fibre periodicity has been determined by H. W. Gonell [22] as 10·4 Å.U.

Natural Silk.

The original results of R. Brill,[23] who obtained good fibre photographs of several varieties of natural silk (Plate I, Fig. 4), are most satisfactorily explained by the suggestion of K. H. Meyer and H. Mark [24] that the fibroin crystallites or micelles are built of extended polypeptide chains consisting for the most part of glycine and alanine residues. The unit of pattern repeats itself along the fibre axis at an interval of almost exactly $2 \times 3{\cdot}5$ Å.U. (see Fig. 2), and the side spacings of the *X*-ray photographs are also in good agreement with what would be expected from parallel chains of amino-acid residues. More recently, O. Kratky [25] has used, instead of natural fibres, the actual secretion in the spinning gland of the silk-worm. By " cold-working " this secretion by stretching and rolling, he has obtained thin films 1—2 m. long and 2—3 mm. wide in which there is a higher degree of crystallite orientation than is found in the fibres (see above). The *X*-ray photographs of such specimens throw further light on the true dimensions of the unit of pattern of fibroin, so that whichever is correct of the possible unit cells put forward, it seems clear that the separation of the parallel polypeptide chains lies somewhere between 4·5 and 6·1 Å.U.

The above remarks refer to the familiar diffraction diagram given by the silk of *Bombyx mori*. The same author has shown, however, that a different *X*-ray pattern is given by the silk of *Thelea polyphemus*, *Satonia*, *Pavonia*, and *Jamamai*. In these cases the fibre period appears to be $7{\cdot}2 \pm 0{\cdot}25$ Å.U. (instead of $6{\cdot}95 \pm 0{\cdot}25$ Å.U. for *Bombyx mori*), but it is not certain, on account of difficulties of measurement, whether this particular deviation is a real one, though

[21] K. Hess and others, *Ber.*, 1928, **61**, 1982; *Z. physikal. Chem.*, [*B*], **4**—**9**.

[22] *Z. Physik*, 1924, **25**, 118; K. H. Meyer and H. Mark, *Ber.*, 1928, **61**, 1936; *A.*, 1924, ii, 588; 1928, 1228.

[23] *Annalen*, 1923, **434**, 204.

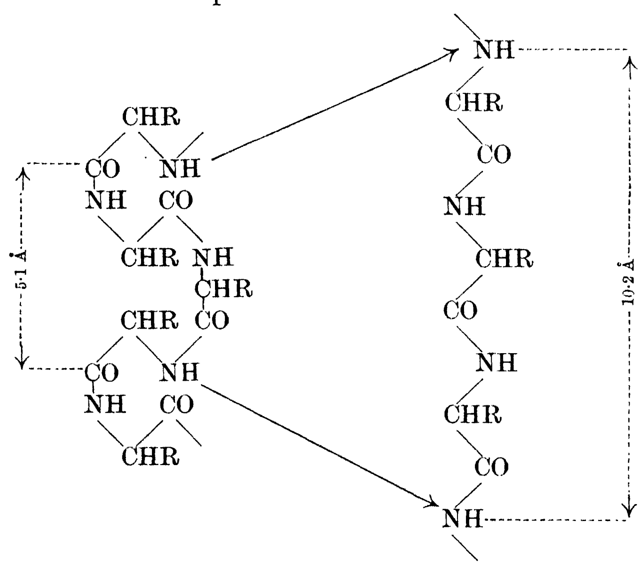
[24] *Ber.*, 1928, **61**, 1932.

[25] *Z. physikal. Chem.*, 1929, [*B*], **5**, 297; O. Kratky and S. Kuriyama, *ibid.*, 1931, [*B*], **11**, 363.

there is no doubt as to the general difference of the fibre pattern of the silk of *Satonia* from that of *Bombyx mori*.

Animal Hairs, etc.

It appears to be now definitely established that animal hairs, together with nails, horn, spines, whale-bone, etc., are built fundamentally from one and the same protein, α-keratin, so named to distinguish it from the extended form of the same protein, β-keratin, which is developed by stretching the natural fibres.[4, 7, 9] In order to account quantitatively for the observed maximum extension, approximately 100%, and the dimensional characteristics of the X-ray photographs of the unstretched and the stretched form, respectively (Plate II, Figs. 5 and 6), the following intramolecular transformation has been put forward :



The details of such a reversible change, that is to say, the correct orientations of the linked units of the main chain and the precise nature of the side chains involved, have yet to be worked out; but the skeleton framework postulated has proved remarkably successful in explaining the basic properties of hair structure. Furthermore, it has thrown light on the properties of proteins in general, inasmuch as it has shown how, by suitable folding of a normal protein chain, ring systems may be formed which are of the nature of diketopiperazine rings,[26] and resistance to chemical attack enhanced by the internal saturation of residual valencies (see below).

[26] N. Troensegaard, *Z. physiol. Chem.*, 1923, **127**, 137.

A striking example of this phenomenon is afforded by the action of steam on animal hairs. It is a well-known fact that stretched hair loses its power of recovery when exposed to steam and becomes " set " in the elongated form (" permanent set " of wool, " permanent wave " of human hair). *X*-Ray analysis shows that this is due to a susceptibility of the extended protein chain (β-keratin) to the attack of steam which is absent in the folded chain (α-keratin). That hair which has been steamed while stretched can no more return to the α-form is shown conclusively by the " fixing " of the β-photograph.

It has now been demonstrated,[4, 9] too, that the normal form of animal hairs which gives rise to the *X*-ray photograph of α-keratin is not in a state of maximum contraction, since it is possible to contract it still to half its original length ! Thus the keratin chain of hair has in reality an extensibility of some 300%—from − 50% to + 100%—and so compares favourably with such an enormously elastic substance as india-rubber.

Another *X*-ray observation in the field of the molecular structure of fibrous epidermal proteins is of peculiar interest for palæontology and evolutionary theory. Hitherto it has been usual to classify feathers and scales with animal hairs, etc., under the heading of keratin. An *X*-ray photograph (Plate II, Fig. 7) shows that this classification is incorrect; that, in fact, the molecular structure of a goose quill, for instance, is quite different from that of the protein which has been described above as α-keratin. The same *X*-ray diffraction pattern as is given by feathers is given also by tortoise-shell, so that the affinity between reptiles and birds and their differentiation from the mammals have now been demonstrated directly by the methods of molecular physics.[27]

Micelle Size.

A classical paper due to M. von Laue [28] gives the general theory of the determination of the dimensions of minute crystals by means of the diffraction of *X*-rays, the possibility of which was first shown by P. Scherrer.[29] As mentioned above, the method depends essentially on the relation between the resolving power of the crystal lattice and the total number of diffracting centres in the lattice. Thus by measuring the broadness of each *X*-ray reflexion we can, after making allowance for the dimensions of the specimen under examination, etc.,[30] estimate the average thickness of the crystallites

[27] T. C. Marwick, *J. Text. Sci.*, 1931, **4**, 31.

[28] *Z. Krist.*, 1926, **64**, 115.

[29] Zsigmondy, " Kolloidchemie," 4 Aufl., 394 ff.

[30] R. Brill, *Z. Krist.*, 1928, **68**, 387; 1930, **75**, 217; R. Brill and H. Pelzer, *Z. tech. Physik*, 1929, **10**, 663; *Z. Krist.*, 1928, **72**, 398; 1930, **74**, 147; J. Böhm and F. Gauter, *ibid.*, 1928, **69**, 17.

perpendicular to each reflecting plane and so build up a fairly complete picture of the shape of the crystallites as a whole. This is probably the most accurate method of estimating the size and shape of colloidal particles at present available. It shows, for example, that the cellulose micelles in ramie are on the average about 55 Å.U. thick but over 600 Å.U. long,[31] which means that the total internal surface of 1 g. of this fibre amounts to 7×10^7 sq. cm.[3] Similarly, Hengstenberg [31] has found 500 Å.U. and 150 Å.U. for the width and thickness, respectively, of the crystallites in stretched rubber, with again a length of over 600 Å.U., results which offer a ready explanation of the fact that these crystallites, in very highly stretched rubber, assume a still more selective orientation than is found in cellulose fibres.[13] Owing to their flatness, the crystallites in highly stretched rubber films lie with their long axes parallel to the axis of stretching and their broader sides roughly parallel to the plane of the film.

The *X*-ray photographs of animal hairs point to dimensions of the same order for the crystallites or micelles of keratin as those found for other textile fibres, but as yet no quantitative results are available by the diffraction method. J. B. Speakman has, however, devised an interesting method, based on ingenious deductions from combined swelling and tensile data, of estimating the micelle size in the wool fibre.[32] He has concluded that the micelles are of the order of 200 Å.U. thick and are separated in the dry fibre by about 6 Å.U., this latter distance being increased to some 40 Å.U. in the water-swollen fibre. Thus, since the micelles are at least ten times as long as they are thick, the total internal surface is of the order of 10^6 sq. cm., and the total amount of intermicellar water adsorbed by wool from saturated air is 20·5% of the dry weight, a value in close agreement with that found from a study by the same author of the effect of water adsorption on the rigidity of wool.

Miscellaneous.

The Molecular Weights of Proteins.[33]—The results of the *X*-ray analysis of protein fibres, such as natural silk and hair, afford evidence of the strongest kind in favour of the peptide chain theory of protein structure. There seems to be little doubt that in these substances long peptide chains are grouped together to form comparatively thin bundles. By analogy with such crystallographic or pseudo-crystallographic groupings of peptide chains, it has now been

[31] J. Hengstenberg, *Z. Krist.*, 1928, **69**, 271; R. O. Herzog and D. Krüger, *J. Physical Chem.*, 1926, **34**, 466.

[32] *Proc. Roy. Soc.*, 1931, [*A*], **132**, 167.

[33] W. T. Astbury and H. J. Woods, *Nature*, 1931, **127**, 663.

proposed that the results of T. Svedberg's investigations [34] of the particle-weights (" molecular weights ") of proteins by means of the ultra-centrifuge can at least be partly explained on the basis of familiar crystallographic theory : for, if we assume that Svedberg's unit " molecular weight " of 34,500 is that of a single protein chain —and the single chains in protein textile fibres appear to have weights of this order—it is then possible to derive the 2-fold, 3-fold, and 6-fold multiples of this weight by arguing that they are simple crystallographic combinations based on the operation of 2-fold and 3-fold symmetry axes. It should be noticed that no second-order symmetry elements, and therefore no enantiomorphous chains, are involved, with the result that the sequence 1, 2, 3, and 6 times 34,500 may be expressed as well-known crystallographic groupings corresponding to the space-groups C_1^1, C_2^1, C_3^2, D_3^3, the last-named being the space-group of quartz.

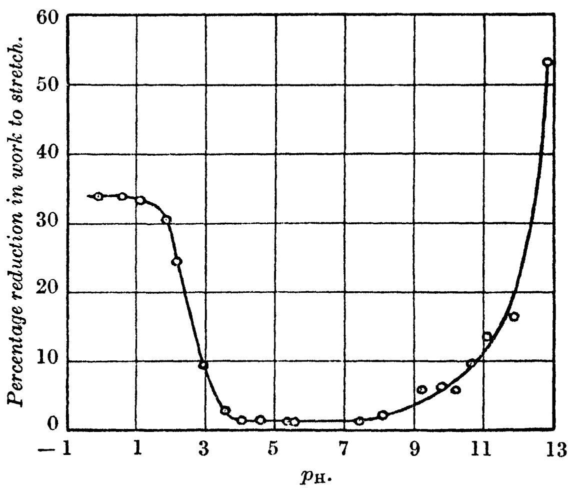
The Denaturation of Proteins.[35]—C. Rimington has suggested that the reversible intramolecular transformation which is undergone by the keratin complex when animal hairs are stretched is probably closely analogous to the tautomeric change which accompanies the denaturation of proteins in general. Denaturation, which can be brought about by both mechanical and chemical agencies, involves loss of solubility at the isoelectric point and some modification of the reactivity of the sulphur groups; but that there is no scission of the molecule is demonstrated by the absence of change in the acid- and base-binding capacity, and in the osmotic pressure. Rimington's deduction from these observations is that denatured proteins are to be classified with *unstretched* hair. In particular, as he points out, affinity for water would be enormously diminished by the rearrangement of peptide linkages into what are virtually closed ring systems. In this connexion, it is interesting to note that stretched hair is definitely in a more reactive state than unstretched hair.[9]

The p_H Stability Region of Insoluble Proteins.—Svedberg's [34] measurements of the stability of a number of soluble proteins as a function of the p_H of the environment have shown that each of the mono-disperse proteins has a fairly wide stability region which includes the isoelectric point. By a totally different technique, Speakman [36] has now shown that the insoluble protein, wool keratin, also conforms to the same rule. The resistance of the wool fibre to extension is far less in either acid or alkaline solution than in distilled water, which gives at once a method for studying the stability of keratin in various media. Speakman has measured the *decrease*

[34] *Kolloid-Z.*, 1930, **51**, 10.
[35] *Nature*, 1931, **127**, 440; *Trans. Faraday Soc.*, 1931, **27**, 222.
[36] *Nature*, 1931, **127**, 665.

in the amount of work required to stretch a wool fibre by 30% of its original length, and has plotted the value so obtained against the p_H of the medium in which the stretching was carried out. The final curve is shown in Fig. 3. It bears a remarkable resemblance to the curves published by Svedberg and obtained by means of the ultracentrifuge, even to the extent that the isoelectric point (at p_H 4·8 for wool [37]) is located, not in the middle of the stability region, but towards the region of lower p_H values. Further details of these important experiments will be found in the original communication : [36] it will be sufficient here to state that Speakman has shown that, from the point of view of p_H stability considerations, the parallel between wool keratin and the proteins studied by Svedberg is strikingly complete.

FIG. 3.



p_H *Stability Curve of Wool Keratin* (*Speakman*).

Mineral Fibres.—In the field of inorganic fibres, *X*-ray analyses of silicate structures which have been carried out chiefly at Manchester by W. L. Bragg [38] and his co-workers have shown that the fibrous silicates, such as asbestos, resemble the organic fibres in that they are also built up of long chains, based in these cases on the linear repetition of certain characteristic silicon–oxygen groupings. The most fundamental unit in silicate structure is a tetrahedron of four oxygen atoms enclosing a silicon atom. The chains which are formed by the repeated linking of such units are in reality gigantic acid radicals held together sideways by the attractions of the metallic ions.

[37] J. B. Speakman, *J. Soc. Dyers Col.*, 1925, **25**, 172.
[38] *Z. Krist.*, 1930, **74**, 237.

X-Ray Investigation of the Structure of a Single Ramie Fibre.—By means of an elegant micro-method devised by Kratky,[39] it is now possible to take *X*-ray fibre photographs of localised areas which are considerably smaller than the cross-section of a single ramie fibre. K. Eckling and O. Kratky [40] have applied this technique to the study of the texture of the single biological cell which constitutes such a fibre, but have failed to obtain photographs substantially different from what is given by the usual macro-investigation of bundles of fibres. From these results, it must be concluded that the micelle orientation throughout the fibre is no higher than the axially symmetrical distribution which has always been met with in previous *X*-ray fibre analyses.

PART II.—ELECTROKINETIC PHENOMENA.

By D. C. HENRY.

UNDER the heading *electrokinesis* is grouped a set of phenomena, originating at the interface between two phases, in which the application of a tangential electric field produces a relative displacement of the two phases, or *vice versa*. The main phenomena included are therefore : *electrophoresis* (cataphoresis), *i.e.*, the motion of suspended particles through a liquid under the action of an applied electric field, together with the converse effect—*electrophoretic* or *migration potential*; and *electrosmosis* (electric endosmose), with the converse effect, *stream potential*, in which the passage of a liquid through a capillary tube or diaphragm is respectively the result or the cause of a potential gradient in the same direction.

In this Report will be reviewed in turn the apparatus and technique employed in investigating these effects, the principal experimental results obtained, and finally the theoretical relationship between electrokinesis and the *electrical double layer*, to the existence of which at interfacial surfaces electrokinetic phenomena are attributed. Since these subjects have only incidentally been referred to in past *Annual Reports*, the present survey will not be restricted to any particular period of years, although in general recent work will receive most attention. For a general description of the phenomena, and for the classical investigations, reference can be made to Smoluchowski's monograph [1] on " Electric Endosmose " or to one of the standard textbooks on Colloids.[2]

[39] *Z. Krist.*, 1930, **73**, 567. [40] *Z. physikal. Chem.*, 1930, [*B*], **10**, 368.

[1] See Graetz, "Handbuch der Elektrizität und des Magnetismus," Bd. 2, p. 379 (Leipzig, 1914); this monograph will be referred to as " Sm."

[2] *E.g.*, H. Freundlich, " Colloid and Capillary Chemistry " (trsl. Hatfield, London, 1926); T. Svedberg, " Colloid Chemistry," 2nd. Ed. (New York, 1928); H. R. Kruyt, " Colloids," 2nd Ed. (New York, 1930).

Apparatus and Technique.

(1) The *electrophoresis* of suspended particles or colloidal solutions has been investigated by three principal methods, *viz.*, the moving-boundary method, the transference method, and the microscopic method.

(*a*) The *moving-boundary method* depends on a determination of the rate of motion, under a known potential gradient, of a horizontal surface of separation of colloidal solution and clear supernatant liquid. The apparatus used is, as a rule, based on the well-known U-tube of E. F. Burton,[3] with or without the addition of wide-bore taps in the limbs [4] designed to facilitate the formation of a sharp boundary; since such taps almost inevitably introduce some irregularity into the bore of the limbs, and a perfect boundary is readily obtainable without their use by sufficiently slow filling of the U-tube from below, they are not to be recommended except where speed of operation is a main consideration. Non-polarisable electrodes have been employed [5] with the object of preventing disturbances by gas evolution and products of electrolysis. The same ends are achieved, in addition to other advantages, by placing the main electrodes in long U-shaped side limbs in which products of electrolysis may accumulate without detriment; subsidiary electrodes (taking negligible current) are fitted in the main vessel near the boundaries, and are used to measure and control the potential fall in the latter.[6]

Several critical discussions of moving-boundary technique have been published, of which that by H. R. Kruyt and P. C. van der Willigen [7] appears especially valuable. Among the points discussed are the disturbances arising from heat generated by the current, uncertainties in the potential gradient at the boundary, and the most suitable composition of the supernatant liquid. Kruyt employs intermicellar fluid, which may be obtained by centrifuging,

[3] *Phil. Mag.*, 1906, [vi], **11**, 436; *A.*, 1906, ii, 275.

[4] A. Coehn, *Z. Elektrochem.*, 1909, **15**, 653; *A.*, 1909, ii, 841; L. Michaelis, *Biochem. Z.*, 1909, **16**, 81; *A.*, 1909, i, 277; F. O. Howitt and E. B. R. Prideaux, *J. Sci. Inst.*, 1930, **7**, 89; *A.*, 1930, 568.

[5] See, *e.g.*, L. Michaelis, ref. (4).

[6] H. R. Kruyt and P. C. van der Willigen, *Kolloid-Z.*, 1928, **44**, 22; *A.*, 1928, 238; S. G. T. Bendien and L. W. Janssen, *Rec. trav. chim.*, 1927, **46**, 739.

[7] Ref. (6); see also H. R. Kruyt, *Kolloid-Z.*, 1925, **37**, 358; *A.*, 1926, 122; T. Svedberg, *Colloid Symposium Monograph*, 1923, 75; J. N. Mukherjee, *Proc. Roy. Soc.*, 1923, [*A*], **103**, 102; *J. Indian Chem. Soc.*, 1928, **5**, 593; *A.*, 1929, 143; L. Engel and W. Pauli, *Z. physikal. Chem.*, 1927, **126**, 247; *A.*, 1927, 511.

ultra-filtration, or coagulation [8] of the sol. Mukherjee [9] gives reasons for preferring to use, in some cases, a suitably chosen electrolyte solution of the same conductivity as the sol. Whichever supernatant liquid is used, a completely uniform potential gradient is both theoretically and experimentally unattainable. Mukherjee [10] attempts to overcome this difficulty by measuring the potential gradient in the neighbourhood of the boundary with the help of small non-polarisable electrodes inserted into the limbs of the electrophoresis tube, while Kruyt [11] shows how the required correction may be made by means of observations on the boundaries in both limbs (incidentally supplying a rational explanation for the frequently observed difference in the speeds of the two boundaries, which was attributed by E. F. Burton [12] to settling under gravity).

The moving-boundary method has been adapted to use with colourless sols, both by employing the Tyndall beam [13] to locate the boundary, and also by photographing the fluorescence of protein sols irradiated by ultra-violet light.[14]

Numerous variations of apparatus have been described, some with a view to biological requirements, others designed primarily for rapid semi-qualitative observations.[15]

The highest precision at present attainable by the moving-boundary method under favourable conditions and with all due precautions would appear to be about ± 2%,[16] but only a few investigations can lay claim to a higher precision than ± 5%, and

[8] F. Powis, *J.*, 1916, **109**, 739; *A.*, 1916, ii, 521; S. W. Pennycuick, *J.*, 1930, 1447; *A.*, 1930, 994.

[9] *J. Indian Chem. Soc.*, 1928, **5**, 593; *A.*, 1929, 143; J. N. Mukherjee, S. P. Rai-Choudhuri, and A. S. Bhattacharyya, *ibid.*, p. 735; *A.*, 1929, 261.

[10] *Proc. Roy. Soc.*, 1923, [*A*], **103**, 102.

[11] Ref. (6).

[12] *Proc. Roy. Soc.*, 1919, [*A*], **95**, 480; *A.*, 1919, ii, 323.

[13] H. R. Kruyt, *Kolloid-Z.*, 1925, **37**, 358; *A.*, 1926, 122; H. R. Kruyt and H. J. C. Tendeloo, *Kolloidchem. Beih.*, 1929, **29**, 413; *A.*, 1929, 1381; A. V. Dumanski and A. G. Kniga, *Kolloid-Z.*, 1926, **39**, 40; *A.*, 1926, 679.

[14] T. Svedberg and E. R. Jette, *J. Amer. Chem. Soc.*, 1923, **45**, 954; *A.*, 1923, i, 614; N. D. Scott and T. Svedberg, *ibid.*, 1924, **46**, 2700; *A.*, 1925, ii, 204; T. Svedberg and A. Tiselius, *ibid.*, 1926, **48**, 2276; A., 1926, 1104.

[15] For examples of biological uses, see C. Todd, *Brit. J. Exper. Path.*, 1927, **8**, 369; F. Vlès, *Arch. Physique biol.*, 1927, **6**, 139; A. P. Krueger, R. C. Ritter, and S. P. Smith, *J. Exp. Med.*, 1929, **50**, 739. For qualitative applications, see W. D. Horne, *Ind. Eng. Chem.*, 1928, **20**, 1147; *A.*, 1929, 44; G. Ettisch and D. Deutsch, *Physikal. Z.*, 1927, **28**, 153; *A.*, 1927, 310; A. Janek, *Kolloid-Z.*, 1924, **34**, 103; *A.*, 1924, ii, 247; R. Fürth, *ibid.*, 1925, **37**, 200; *A.*, 1925, ii, 1057. A U-tube apparatus for use with oil emulsions has been described by H. Limburgh, *Rec. trav. chim.*, 1926, **45**, 854.

[16] See, *e.g.*, H. R. Kruyt and P. C. van der Willigen, ref. (6); J. N. Mukherjee, S. P. Rai-Choudhuri, and A. N. Rao, *J. Indian Chem. Soc.*, 1928, **5**, 697; *A.*, 1929, 261.

it is quite uncertain how far either of these limits represents the accuracy of determination of a true electrophoretic velocity.

(*b*) The *transference method* depends on the same principles as the determination of an ionic transport number by Hittorf's method. The apparatus may consist of two (or three) vessels connected by syphons,[17] of a two-compartment tube as used for ionic transport numbers,[18] or of a U-tube apparatus,[19] similar to that used in the moving-boundary method, arranged to prevent access of the colloid to the electrodes.

Engel and Pauli claim a precision of $\pm$ 2%, and Paine one of $\pm$ 5% by the transference method. This method has the advantage of eliminating the uncertainty in the potential gradient which is the chief difficulty in the moving-boundary method. Its own limit is probably set by analytical considerations.

(*c*) The *microscopic method* differs from those described above in that the motion of individual particles is observed in the microscope or ultramicroscope, which is a considerable advantage for theoretical studies. On the other hand, it is inapplicable to concentrated or amicroscopic sols, and, in consequence of the Brownian movement, can only be expected to give representative results by the observation of large numbers of particles. P. Tuorila [20] has shown that the indivual observations conform to Gauss's law of errors, and hence calculates the number of observations required to secure a given degree of precision in the mean. For a general description of the method, reference may be made to Smoluchowski's monograph [21] or to one of the text-books cited. A general discussion of the method has been given by Kruyt.[22] Observations are usually made by timing particles across a pair of eyepiece cross-wires, but two alternative methods, one involving photographic registration,[23] the other the use of alternating applied potentials,[24] have been described, and appear to have decided advantages over the more usual method. A rotating electric field has also been employed.[25]

[17] G. Varga, *Kolloidchem. Beih.*, 1919, **11**, 3; *A.*, 1921, ii, 371; R. Wintgen, *Z. physikal. Chem.*, 1922, **103**, 238; *A.*, 1923, ii, 78; H. H. Paine, *Trans. Faraday Soc.*, 1928, **24**, 412; *A.*, 1928, 1093.

[18] R. Wintgen and M. Biltz, *Z. physikal. Chem.*, 1923, **107**, 403; *A.*, 1924, ii, 156; R. Wintgen and H. Löwenthal, *ibid.*, 1924, **109**, 378; *A.*, 1924, ii, 534.

[19] L. Engel and W. Pauli, ref. (7); J. W. McBain and R. C. Bowden, *J.*, 1923, **123**, 2417.

[20] *Kolloid-Z.*, 1928, **44**, 11; *A.*, 1928, 235.

[21] Sm., p. 382.

[22] Refs. (6) and (7).

[23] T. Svedberg and H. Anderson, *Kolloid-Z.*, 1919, **24**, 156; *A.*, 1919, ii, 315.

[24] *Idem, ibid.*; O. Blüh, *ibid.*, 1925, **37**, 267; *Ann. Physik*, 1926, **79**, 143; *A.*, 1926, 23, 576.

[25] E. M. Pugh and C. A. Swartz, *Physical Rev.*, 1930, **36**, 1495; *A.*, 1931, 36.

Electrophoresis cells have been described by: T. Svedberg,[26] H. R. Kruyt,[27] P. Tuorila [28] (rectangular cemented cells with platinum electrodes); H. R. Kruyt and A. E. van Arkel [29] (as above, but electrodes arranged to render gas evolution innocuous); K. van der Grinten [30] (rectangular cell, partially open, quick in use, platinum electrodes); S. Mattson [31] (circular section all-glass cell, easily cleaned and filled, platinum electrodes); J. H. Northrop,[32] M. Kunitz [33] (rectangular cemented cell, non-polarisable electrodes); J. H. Northrop and M. Kunitz,[34] H. Abramson [35] (cell drawn from glass tube to flat section, easily cleaned and filled, non-polarisable electrodes). Extreme cleanliness is essential, and the all-glass cells are preferable to those with cemented joints. Unfortunately none of the all-glass cells hitherto described has a true rectangular cross-section, which in certain circumstances (see below) is most desirable.

The observed velocities of the particles are compounded of the true electrophoretic velocity and the streaming motion of the liquid set up by electrosmosis at the cell walls. With a closed cell, the streaming motion is in one direction near the walls, and in the opposite direction in the centre of the cell. For a cell whose depth is small compared with its width, R. Ellis [36] and M. Smoluchowski [37] have shown how the two velocities may be disentangled by means of observations made at different depths in the cell; for such cells the precise form of the *narrow* sides is immaterial, and certain patterns of all-glass cells are suitable. With deeper cells such as are desirable for use with the slit ultramicroscope, Smoluchowski's calculation is not valid, while Ellis's method of correction, though in theory applicable, is impossibly cumbersome in practice; instead, the correction needs to be calculated by the formulæ published by C. G. Sumner and D. C. Henry,[38] which are valid for any ratio of depth to width, but require the cross-section to be strictly rectangular. The use of either method of correction presupposes a completely closed cell, and one cannot *a priori* assume the process to be applicable to a cell such as van der Grinten's. It appears, however,

[26] *Nova Acta (Upsala)*, 1907, [iv], **2**, No. 1, 149; *Kolloid-Z.*, 1919, **24**, 156.
[27] *Ibid.*, 1916, **19**, 161.
[28] Ref. (20). [29] *Kolloid-Z.*, 1923, **32**, 91; *A.*, 1923, ii, 226.
[30] *Compt. rend.*, 1924, **178**, 2083; *J. Chim. physique*, 1926, **23**, 226; *A.*, 1924, ii, 664; 1926, 467.
[31] *J. Physical Chem.*, 1928, **32**, 1532; *A.*, 1928, 1323.
[32] *J. Gen. Physiol.*, 1922, **4**, 629. [33] *Ibid.*, 1924, **6**, 413.
[34] *Ibid.*, 1925, **7**, 729. [35] *Ibid.*, 1929, **12**, 469; *A.*, 1929, 478.
[36] *Z. physikal. Chem.*, 1911, **78**, 321; *A.*, 1912, ii, 13.
[37] *Op. cit.*, p. 382.
[38] *Proc. Roy. Soc.*, 1931, [*A*], **133**, 130; *A.*, 1232.

from his results, as recalculated by H. Abramson,[39] that the surface tension at the open ends is sufficient to prevent any bodily displacement of the liquid, so that Smoluchowski's formula may be applicable; van der Grinten's own method of calculation,[40] based on his claim that the streaming velocity is zero in the centre of the cell, is, as Abramson shows, based on a misinterpretation of his results, and is almost certainly erroneous. To avoid these complications, M. Mooney [41] has devised a cell in which the return flow takes place in an auxiliary and much wider tube; the flow in the observational tube is then sensibly constant over the whole cross-section, which simplifies comparative observations.

Vertical electrophoresis tubes have also been used for the investigation of the movement of gas bubbles and oil drops,[42] the electrophoretic force being directly compared with the gravitational force by methods analogous to those employed by Millikan with oil drops in air. For the same purpose there have been employed [43] horizontal circular tubes which are kept in rotation about a horizontal axis in order to maintain the bubble or drop on the axis of the tube.

The precision of the microscopic method probably exceeds that of all but the best determinations by the other two methods, and may be better than $\pm$ 2%.

(*d*) *Miscellaneous electrophoretic methods.* Qualitative [44] and quantitative [45] electrophoretic investigations have been made by observation of the deflexion of a suspended fibre or needle in the electric field. Other methods employed include the motion of a single drop of mercury [46] and the lateral deflexion of a stream of mercury droplets [47] or of a jet of colourless sol; [48] in the latter case

[39] *J. Physical Chem.*, 1931, **35**, 289; *A.*, 429.

[40] Also adopted by H. R. Kruyt and G. S. de Kadt, *Kolloidchem. Beih.*, 1931, **32**, 249; *A.*, 796.

[41] *Physical Rev.*, 1927, **29**, 218; *A.*, 1928, 1315.

[42] *Idem, ibid.*, 1924, **23**, 396; J. W. McBain and R. C. Williams, *Colloid Symposium Annual*, 1930, 105; D. A. Newton, *Phil. Mag.*, 1930, [vii], **9**, 769; *A.*, 1930, 858.

[43] H. A. McTaggart, *ibid.*, 1914, [vi], **27**, 297; **28**, 367; 1922, [vi], **44**, 387; *Trans. Roy. Soc. Canada*, 1924, **18**, iii, 129; *A.*, 1914, ii, 762; 1925, ii, 509; T. Alty, *Proc. Roy. Soc.*, 1924, [*A*], **106**, 315; 1926, [*A*], **110**, 178; *A.*, 1926, 239; B. W. Currie and T. Alty, *ibid.*, 1929, [*A*], **122**, 622; *A.*, 1929, 390.

[44] P. A. Thiessen, *Z. anorg. Chem.*, 1929, **181**, 379; F. Fairbrother and F. Wormwell, *J.*, 1928, 1991; *A.*, 1928, 1097; A. Garrison, *J. Amer. Chem. Soc.*, 1923, **45**, 37; *A.*, 1923, ii, 115.

[45] C. G. Sumner and D. C. Henry, ref. (38).

[46] S. Bodforss, *Z. Elektrochem.*, 1923, **29**, 121.

[47] A. Frumkin, *J. Russ. Phys. Chem. Soc.*, 1917, **49**, 207.

[48] R. H. Humphry, *Kolloid-Z.*, 1926, **38**, 306; *A.*, 1926, 577; R. H. Humphry and R. S. Jane, *Trans. Faraday Soc.*, 1926, **22**, 420; *A.*, 1926, 1204; E. A. Lantz and O. A. Pickett, *Ind. Eng. Chem.*, 1930, **22**, 1309.

the jet was made visible by means of the Töpler "schlieren Effekt."

(2) *Electrophoretic Currents.*—When particles are allowed to fall, or bubbles to rise, through a liquid, under the action of gravity, a potential gradient is set up in the liquid parallel to the direction of motion. This phenomenon, the converse of electrophoresis, has so far only led to qualitative results. The classical investigations are those of Dorn, Makelt, Billiter, and Stock.[49] The only recent investigations have been published by E. F. Burton and J. E. Currie [50] and by R. D. Kleeman and C. R. Pitts.[51]

(3) *Electrosmosis.*—For a full account of the earlier work in this field, reference should be made to Smoluchowski's monograph.[52] For the investigation of electrosmosis through diaphragms (whether in the form of a membrane or of a plug of powder) almost all forms of apparatus are in principle based on that of J. Perrin,[53] in which the passage of liquid through the diaphragm is indicated by the motion of a meniscus in a capillary tube connected to the vessel on one side of the diaphragm. The most notable modification is that of Briggs,[54] who connected the capillary so as to serve as a return path for the liquid; a bubble in the capillary serves to indicate the electrosmotic flow. Platinum electrodes were used, and consequently the apparatus had to be open to the air to allow for the escape of evolved gases. A. Gyemant [55] and F. Fairbrother and H. Mastin [56] employ non-polarisable electrodes which allow the apparatus to be constructed as a closed system.

The potential fall across the diaphragm has been calculated by most workers in terms of the total current flowing, the specific conductivity of the liquid, and the "effective dimensions" of the diaphragm; the last magnitude is determined by calibration with a liquid of known conductivity. Fairbrother and Mastin point out that this mode of calculation assumes the conductivity of the liquid in the pores of the diaphragm to be identical with that of the liquid in bulk, which is known both theoretically [57] and experimentally [58] not to be the case. These authors therefore use sub-

[49] See Sm., p. 385.

[50] *Phil. Mag.*, 1925, [vi], **49**, 194; *A.*, 1925, ii, 531.

[51] *J. Physical Chem.*, 1925, **29**, 508; *A.*, 1925, ii, 659.

[52] *Op. cit.*, pp. 366, 388, 401.

[53] *J. Chim. physique*, 1904, **2**, 601; 1905, **3**, 50; *A.*, 1905, ii, 138.

[54] T. R. Briggs, H. S. Bennett, and H. L. Pierson, *J. Physical Chem.*, 1918, **22**, 256; *A.*, 1918, ii, 214. See also A. Strickler and J. H. Mathews, *J. Amer. Chem. Soc.*, 1922, **44**, 1647; *A.*, 1922, ii, 688.

[55] *Z. physikal. Chem.*, 1922, **103**, 260; *A.*, 1923, ii, 52.

[56] *J.*, 1924, **125**, 2319; *A.*, 1925, ii, 47.

[57] Sm., p. 396.

[58] F. Fairbrother, *J.*, 1924, **125**, 2495; *A.*, 1925, ii, 129.

sidiary non-polarisable electrodes to make a direct determination of the potential fall across the diaphragm. Another source of error in the usual electrosmotic technique arises from the fact that, owing partly to viscosity and partly to surface tension, a quite appreciable pressure difference between the two ends of the apparatus is required to move the bubble in the capillary. This difference causes a certain amount of back flow through the diaphragm, with the result that the electrosmotic flow per unit current, which should be independent of the permeability of the diaphragm, is found to diminish as the permeability increases.[59] The error is minimised by using as wide a capillary as is consistent with the sensitivity required, by ensuring absolute freedom from grease, and by avoiding the use of unduly permeable diaphragms.[60] The error may be allowed for by determining either the pressure required to move the bubble in a blank experiment, or the pressure difference established during the electrosmotic flow experiment, a differential manometer being used.[61]

The reproducibility attainable in electrosmotic experiments is, under specially favourable conditions, with well-defined diaphragms and pure liquids, as high as $\pm$ 1%; [62] with solutions, and especially with diaphragms liable to vary in packing, it is certainly much lower.

(4) The method of *stream potential* [63] has been applied in the main (though not exclusively) to investigations with capillary tubes of glass or quartz, and is carried out by forcing liquid from one vessel to another under a well-defined and constant pressure difference which is, as a rule, provided by a compressed gas. The potential difference produced is measured by a compensation method with the help of metallic or non-polarisable electrodes in, or connecting with, the terminal vessels. Typical forms of apparatus are described by H. R. Kruyt and P. C. van der Willigen,[64] H. Freundlich and P. Rona,[65] and H. Lachs and J. Biczyk.[66] The last-named workers found that a great improvement in reproducibility resulted from a careful shielding from electrostatic influences of all parts of the compensation circuit, and from a thorough control of the carbon

[59] See, *e.g.*, A. Strickler and J. H. Mathews, ref. (54); J. N. Mukherjee and P. Kundu, *J. Indian Chem. Soc.*, 1926, **3**, 335; *A.*, 1927, 409.

[60] F. Fairbrother and M. Balkin, *J.*, 1931, 389; *A.*, 434.

[61] Unpublished experiments made in the Reporter's laboratory show that the error due to back pressure may be considerable, and that the two methods suggested for applying a correction give concordant results, the latter being the more trustworthy.

[62] In this connexion, see F. Fairbrother and H. Varley, *J.*, 1927, 1584; *A.*, 1927, 826; H. C. Hepburn, *Proc. Physical Soc.* 1926, **38**, 363; *A.*, 1926, 1100.

[63] See Sm., pp. 372, 378. [64] *Kolloid-Z.*, 1928, **45**, 307; *A.*, 1928, 1091.

[65] *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1920, **20**, 397.

[66] *Z. physikal. Chem.*, 1930, [*A*], **148**, 441; *A.*, 1930, 1119.

dioxide content of the water used, to variations in which the electrokinetic potential is very sensitive. It is further essential [67] that the rate of flow employed should lie well below the limit at which Poiseuille's law ceases to hold. With these precautions results are obtainable with a given capillary which are reproducible to within 2% both in pure water and in electrolyte solutions.

Stream-potential measurements have also been carried out with porous diaphragms; typical forms of apparatus are described by D. R. Briggs [68] and by W. McK. Martin and R. A. Gortner.[69]

Mention must be made of a special technique by which the electrokinesis of *proteins* may be more easily investigated than by the methods employing the Tyndall beam or fluorescence in ultra-violet light. It has been shown [70] that many solids adsorb a layer of protein from aqueous solution and behave electrokinetically like particles of protein. This has been applied to electrophoresis by the micoscopic method, with particles of glass or quartz,[71] to the moving-boundary method with colloidal gold particles,[72] and to the stream-potential method with a quartz capillary.[73] Results are obtained which are concordant among themselves and with those obtained by the fluorescence method.

Experimental Results.

The observational data of electrokinetic investigations are quantities such as "the electrophoretic velocity under unit potential gradient," "the electrosmotic flow per coulomb," or "the stream potential per atmosphere pressure difference"; in view of uncertainties in the theoretical interpretation of these data, J. W. McBain [74] has strongly urged that the results of electrokinetic researches should be recorded in terms of the observed magnitudes only. While it is undoubtedly highly desirable that the latter should invariably be included in the published report to facilitate

[67] See, *e.g.*, H. R. Kruyt and P. C. van der Willigen, ref. (64); H. Freundlich and G. Ettisch, *Z. physikal. Chem.*, 1925, **116**, 401; *A.*, 1925, ii, 873.

[68] *J. Physical Chem.*, 1928, **32**, 641; *A.*, 1928, 713.

[69] *Ibid.*, 1930, **34**, 1509; *A.*, 1930, 1124.

[70] H. Davis, *J. Physiol.*, 1922, **57**, 16; H. Freundlich and H. Abramson, *Z. physikal. Chem.*, 1928, **133**, 51; *A.*, 1928, 587; H. Abramson, *J. Amer. Chem. Soc.*, 1928, **50**, 390; *A.*, 1928, 364; *Colloid Symposium Monograph*, 1928, 115; *J. Gen. Physiol.*, 1930, **13**, 169, 657; *A.*, 1930, 1250; *J. Physical Chem.*, 1931, **35**, 289; *A.*, 429.

[71] H. Abramson, ref. (70).

[72] E. B. R. Prideaux and F. O. Howitt, *Proc. Roy. Soc.*, 1929, [*A*], **126**, 126; *A.*, 1930, 159.

[73] D. R. Briggs, *J. Amer. Chem. Soc.*, 1928, **50**, 2358; *A.*, 1928, 1193.

[74] *J. Physical Chem.*, 1924, **28**, 706; *A.*, 1924, ii, 594; *Colloid Symposium Monograph*, 1926, 7.

re-interpretation in the event of any alteration in the theoretical point of view, it would appear inconvenient and cumbersome entirely to avoid discussion in terms of the current theories, provided that the underlying assumptions are recognised; in this Report, therefore, we shall follow the usual practice and adopt the commonly accepted interpretations of electrokinesis, based on the theories of Helmholtz and Smoluchowski,[75] bearing in mind the probability that these may require modification in the future. On these theories the observational data in question are related by simple formulæ [76] to a magnitude known as the "electrokinetic potential" (designated ζ), and it is to an evaluation and interpretation of this quantity, and of its variation with conditions, that the majority of electrokinetic investigations are directed.

The ζ-Potential at the Interface between Pure Phases.—Coehn's rule,[77] which states that, of two dielectrics in contact, that with the higher dielectric constant is charged positively, is not confirmed by recent investigations, though there are indications of a more fundamental generalisation of which it may in certain circumstances be the manifestation. A. Strickler and J. H. Mathews,[78] and more recently W. McK. Martin and R. A. Gortner,[79] have investigated the ζ-potential at the interface cellulose–organic liquid. The former authors conclude that the magnitude of the electrokinetic effect, but not its sign, is roughly determined by the dielectric constants, while both investigations lead to the conclusion that the orientation of polar molecules at the interface is a determining factor. This idea gains quantitative support from the work of F. Fairbrother and M. Balkin,[80] who find that of the 14 liquids used by them for which dipole moments are known, ζ for all but one (acetone) is a linear function of the dipole moment multiplied by the molar surface area; in agreement with this, the non-polar liquids benzene and carbon tetrachloride give zero electrosmosis. The non-zero result obtained by Strickler and Mathews with benzene they attribute to impurities in the benzene. F. Fairbrother and F. Wormwell [81] have made qualitative observations of the electrokinetic potential of solids against their own melts; all the solids investigated (except *o*-chlorophenol and benzene, which gave zero results) were found to be positive against the corresponding liquids. It is not certain whether this is in contradiction to Coehn's rule or not, as there is considerable uncertainty about the dielectric constants of solids at their melting points.

[75] H. von Helmholtz, *Wied. Ann.*, 1879, **7**, 357; "Gesamm. Abhandl." ii, p. 855; Sm., p. 379; M. von Smoluchowski, *Krakau Anzeiger*, 1903, p. 182.
[76] See p. 349. [77] Sm., p. 401. [78] Ref. (54).
[79] Ref. (69). [80] Ref. (60). [81] Ref. (44).

The Influence of Electrolytes in Aqueous Solution on the ζ-Potential.—The older views on this subject may be summed up in the generalisations: (1) The ion of opposite sign to the charge on the solid phase has a preponderating influence, and tends to lower the numerical value of ζ; (2) the efficacy of an ion in influencing the value of ζ increases with its valency and with its adsorbability.

The evidence for the general truth of the "valency effect" is ample; reference may be made to the text-books, and among numerous more recent papers to those of H. Freundlich and H. P. Zeh,[82] F. Fairbrother and H. Mastin,[83] and H. R. Kruyt and P. C. van der Willigen.[84]

The evidence for the "adsorbability effect" is more equivocal, since the electrokinetic effect is sometimes taken as a measure of adsorbability;[85] at the same time it is just those ions which on other grounds are known, or by analogy may be expected, to be strongly adsorbed, which exert an influence on ζ greater than is to be anticipated from their valency; examples are hydrogen, hydroxyl, heavy-metal, complex, and organic ions, especially those of high molecular weight.[86]

The first generalisation has required considerable modification. Limiting ourselves, for simplicity of discussion, to the case of a negatively charged solid phase, we find, in the first place, that salts of a univalent kation frequently cause in low concentration an increase[87] in the numerical value of ζ, to be followed in higher concentrations only by the decrease which is to be expected if the "ion of opposite charge" exerts the preponderating influence. This is more particularly the case when the anion is of high valency or adsorbability, as, *e.g.*, FeC_6N_6'''' with arsenious sulphide sol,[88]

[82] *Z. physikal. Chem.*, 1924, **114**, 65; *A.*, 1925, ii, 115.

[83] *J.*, 1925, **127**, 322; *A.*, 1925, ii, 302.

[84] *Kolloid-Z.*, 1928, **45**, 307; *A.*, 1928, 1091.

[85] See, *e.g.*, J. N. Mukherjee and H. L. Ray, *J. Indian Chem. Soc.*, 1924, **1**, 173; *A.*, 1925, ii, 385; J. N. Mukherjee and P. Kundu, *ibid.*, 1926, **3**, 335; *A.*, 1927, 409.

[86] See, *e.g.*, H. R. Kruyt and P. C. van der Willigen, ref. (84); J. N. Mukherjee and B. C. Roy, *J.*, 1924, **125**, 476; *A.*, 1924, ii, 313; C. E. A. Winslow and E. H. Fleeson, *J. Gen. Physiol.*, 1926, **8**, 195; *A.*, 1926, 324; P. Tuorila, *Kolloidchem. Beih.*, 1928, **27**, 44; *A.*, 1928, 950; D. R. Briggs, *J. Physical Chem.*, 1930, **34**, 1326.

[87] See, *e.g.*, H. R. Kruyt, *Kolloid-Z.*, 1918, **22**, 81; *A.*, 1918, ii, 289; H. C. Hepburn, *Proc. Physical Soc.*, 1926, **38**, 363; *A.*, 1926, 1100; A. Ivanitzkaja and M. Proskurnin, *Kolloid-Z.*, 1926, **39**, 15; *A.*, 1926, 679; L. Orlova, *Z. physikal. Chem.*, 1928, **134**, 345; *A.*, 1928, 701; A. von Buzágh, *Kolloid-Z.*, 1929, **48**, 33; **49**, 35; *A.*, 1929, 763, 1236; H. Lachs and J. Biczyk, *Z. physikal. Chem.*, 1930, [*A*], **148**, 441; *A.*, 1930, 1119.

[88] H. Freundlich and H. P. Zeh, ref. (82).

or hydroxyl with manganese oxide,[89] platinum,[90] kaolin,[91] and glass.[92] In the second place, we commonly find that the nature of the anion has quite a considerable influence on the form of the ζ–c curve over the whole range of concentrations.[93] Similar conclusions hold, *mutatis mutandis*, for positively charged solids. It would thus appear that modification of the ζ-potential is caused not merely by adsorption of the ion of opposite charge, a process which is easily understandable since it can be attributed to simple electrostatic attraction, but also by adsorption of the ion of like charge, which is not so readily explicable. The ability of a charged surface to adsorb ions of like charge is further exemplified by the frequency with which a multivalent or strongly adsorbed kation is able not only to reduce the ζ-potential of a negative surface to zero, but even to reverse it;[94] the ions which accomplish this latter feat would seem necessarily to be adsorbed in opposition to electrostatic forces. This is, of course, not impossible, for there certainly exist modes of adsorption which are not directly electrostatic in origin, but it must not be forgotten that a change in the ζ-potential is not inevitably bound up with a corresponding change in the electric charge on the solid phase.[95]

In experiments with a salt-like solid, the solubility of the salt which may be formed by an ion of the added electrolyte with one of the ions of the solid appears to have a considerable influence on the apparent adsorbability.[96]

[89] B. Ghosh, *J.*, 1926, 2605; *A.*, 1926, 1203.

[90] S. W. Pennycuick, *J.*, 1930, 1447; *A.*, 1930, 994.

[91] A. Reifenberg, *Kolloid-Z.*, 1930, **53,** 162.

[92] H. R. Kruyt and P. C. van der Willigen, ref. (84).

[93] See, *e.g.*, J. N. Mukherjee and H. L. Ray; J. N. Mukherjee and P. Kundu, ref. (85); J. N. Mukherjee and S. G. Chaudhury, *J. Indian Chem. Soc.*, 1925, **2,** 296; *A.*, 1926, 352; J. Glixelli and J. Wiertelak, *Kolloid-Z.*, 1927, **43,** 85; 1928, **45,** 197; *A.*, 1927, 1139; 1928, 953; A. Rabinerson, *ibid.*, 1928, **45,** 122; *A.*, 1928, 833.

[94] See, *e.g.*, A. Boutaric and G. Perreau, *Compt. rend.*, 1927, **184,** 814; *A.*, 1927, 410; B. Ghosh, ref. (89); J. N. Mukherjee and B. C. Roy, P. Tuorila, C. E. A. Winslow and E. H. Fleeson, ref. (86); A. von Buzágh, ref. (87); S. W. Pennycuick, ref. (90); F. Fairbrother and H. Mastin, ref. (83); A. J. Stamm, *Colloid Symposium Monograph*, 1928, 361; *A.*, 1929, 759; H. Limburgh, *Rec. trav. chim.*, 1926, **45,** 854; *A.*, 1927, 109.

[95] Thus, *e.g.*, H. R. Kruyt, A. C. W. Roodvoets, and P. C. van der Willigen (*Colloid Symposium Monograph*, 1926, 304; *A.*, 1928, 17) attribute a rising electrophoresis curve to changes in the dielectric constant, while A. J. Rabinovitsch and E. B. Fodimann (*Z. physikal. Chem.*, 1931, **154,** 255; *A.*, 682) attribute the same effect to alterations in the structure of the electrical double layer brought about by interchange adsorption.

[96] J. N. Mukherjee and H. L. Ray; J. N. Mukherjee and P. Kundu; ref. (85).

With proteins, as might be expected from their amphoteric nature, the hydrogen-ion concentration of the solution has a preponderating effect, and not a great deal is known about the effects of other ions. Reference may be made to publications already cited [97] and to the numerous papers of J. Loeb.[98]

Closely related to the subject matter of this section is the study of the influence of *dilution* on the ζ-potential. Increase,[99] decrease,[1] and even reversal [2] of ζ has been observed to take place on dilution of a colloidal solution. These effects are presumably due to a readjustment of the electrolyte adsorption equilibrium between colloidal particle and medium, and the result obtained will depend on the shape of the ζ–c curve and on the initial electrolyte content; for example, a silver iodide [3] sol prepared in the presence of excess silver nitrate is positive, whilst silver iodide is negative to pure water; dilution of the former sol naturally therefore leads to a reversal of the sign of ζ.

The Influence of Non-electrolytes on the ζ-Potential.—This has been the subject of a few investigations. Alcohols, acetone, urea, and cane sugar in considerable concentration [4] reduce the electrophoretic velocity (v) in all cases examined; in general, the same applies to the magnitudes [5] $\eta v/D$ (proportional to ζ) and ηv (proportional to the surface charge in an electrical double layer of constant thickness). A variation in the structure of the double layer therefore appears to be indicated.[6] An extensive investigation [7] has recently been carried out using quartz powder with quite dilute aqueous solutions of various alcohols, amines, and fatty acids. The electrophoretic velocity is lowered by the acids and the four lowest aliphatic alcohols, but raised by amyl and hexyl alcohols and by both aromatic and aliphatic amines—by the latter in surprisingly low concentration.

[97] Refs. (13), (71), (72), and (73).

[98] *J. Gen. Physiol.*, 1919—1923.

[99] S. S. Bhatnagar and D. C. Bahl, *Kolloid-Z.*, 1930, **50**, 48; *A.*, 1930, 291; I. Remesov, *Biochem. Z.*, 1930, **218**, 86; *A.*, 1930, 415.

[1] J. N. Mukherjee, S. G. Chaudhury, and S. P. Rai-Choudhuri, *J. Indian Chem. Soc.*, 1927, **4**, 493; *A.*, 1928, 15.

[2] H. R. Kruyt and P. C. van der Willigen, *Z. physikal. Chem.*, 1928, [*A*], **139**, 53; *A.*, 1929, 136; A. Lottermoser and W. Riedel, *Kolloid-Z.*, 1930, **51**, 30; *A.*, 1930, 696.

[3] H. R. Kruyt and P. C. van der Willigen, ref. (2).

[4] S. S. Bhatnagar and D. C. Bahl, ref. (99); J. N. Mukherjee, S. G. Chaudhury, and S. P. Rai-Choudhuri, ref. (1), see above; J. N. Mukherjee, S. P. Rai-Choudhuri, and A. N. Rao, *J. Indian Chem. Soc.*, 1928, **5**, 697; *A.*, 1929, 261.

[5] η is the viscosity and D the dielectric constant.

[6] See G. Ettisch and A. Zwanzig, *Z. physikal. Chem.*, 1930, [*A*], **147**, 151; *A.*, 1930, 697.

[7] S. H. Whang, *Kolloidchem. Beih.*, 1931, **32**, 169; *A.*, 429.

In the presence of non-electrolytes, the ζ–c curves for electrolyte additions are modified in form.[8]

The Effect on Electrophoresis of Irradiation.—This has been examined with visible and ultra-violet light [9] and with X-rays,[10] and found to be small or non-existent.

Surface Conductivity.—It was predicted by Smoluchowski [11] that the existence of an electrical double layer at an interface must give rise to the phenomenon of surface conductivity. This was confirmed by Stock,[12] and has recently been observed by several workers; [13] in the last-quoted paper Smoluchowski's theoretical relation between the surface conductivity and the ζ-potential is employed to calculate relative values for the thickness of the double layer and for the fixed charge. Some recent experiments [14] throw considerable doubt on the validity of the relation in question, since for glass in contact with a solution of hydrogen chloride in dry benzene, *cyclo*hexane, and carbon tetrachloride, there was no correlation between the surface conductivity and the ζ-potential. The carbon tetrachloride solution, for example, which gave much the greatest surface conductivity, showed zero electrosmosis at all concentrations of hydrogen chloride.

The Electroviscous Effect.—M. von Smoluchowski [15] showed that the apparent viscosity of a suspension of charged particles should be greater than that of a similar suspension of uncharged particles, and deduced a relationship between this "electroviscous effect" and the ζ-potential. The former has been studied in both lyophilic [16] and lyophobic [17] sols, and provides a valuable method for studying changes in the ζ-potential in cases not readily amenable to ordinary electrokinetic technique.

Electrokinesis and the Stability of Colloidal Solutions.—That a

[8] J. N. Mukherjee, S. P. Rai-Choudhuri, and A. N. Rao, ref. (4), p. 347.

[9] K. Schaum and P. Friederich, *Z. wiss. Phot.*, 1924, **23**, 98.

[10] S. S. Bhatnagar, R. S. Gupta, K. G. Mathur, and K. N. Mathur, *Z. Physik*, 1929, **56**, 684; D. A. Newton, *Phil. Mag.*, 1930, [vii], **9**, 769.

[11] Sm., p. 396.

[12] Sm., p. 398.

[13] F. Fairbrother, *J.*, 1924, **125**, 2495; *A.*, 1925, ii, 129; J. W. McBain, C. R. Peaker, and A. M. King, *J. Amer. Chem. Soc.*, 1929, **51**, 3294; *A.*, 1930, 37; J. W. McBain and C. R. Peaker, *J. Physical Chem.*, 1930, **34**, 1033; *A.*, 1930, 704; H. B. Bull and R. A. Gortner, *ibid.*, 1931, **35**, 309; *A.*, 435.

[14] F. Fairbrother and M. Balkin, *J.*, 1931, 1564; *A.*, 914.

[15] *Kolloid-Z.*, 1916, **18**, 190.

[16] H. R. Kruyt and H. G. Bungenberg de Jong, *Z. physikal. Chem.*, 1922, **100**, 25; *Kolloidchem. Beih.*, 1928, **28**, 1; H. G. Bungenberg de Jong, *Rec. trav. chim.*, 1924, **43**, 189; R. H. Humphry and R. S. Jane, *Trans. Faraday Soc.*, 1926, **22**, 420; *Kolloid-Z.*, 1927, **41**, 293; B. J. Holwerda, *Rec. trav. chim.*, 1928, **47**, 248; H. J. C. Tendeloo, *ibid.*, 1929, **48**, 23.

[17] *Idem, Kolloid-Z.*, 1927, **41**, 290; N. R. Dhar and S. Ghosh, *ibid.*, 1929, **48**, 43.

relationship exists between the stability of lyophobic sols and the charge on the colloidal particle is undoubted, the general view being that a sol becomes unstable when the ζ-potential is reduced below a certain "critical potential."[18] This generalisation appears to be valid in many cases, but apparently fails when the coagulating ion is of low valency and adsorbability. Space does not permit a discussion of the considerable volume of work which has been done on this problem of stability and the critical potential; some of the most prominent among recent publications on the subject are referred to.[19]

The Theory of Electrokinesis.

Helmholtz's well-known theory of electrokinesis [20] was based on the suggestion made by Quincke that there exists at the interface between two phases an "electrical double layer" consisting of two laminar distributions of electrification, equal in amount but opposite in sign, forming a kind of parallel plate condenser of which the "inner sheet" is firmly attached to the rigid phase, while the "outer sheet" resides in the mobile phase. This theory, with a slight modification introduced by Pellat, was extended and generalised by Smoluchowski,[20] and leads to the fundamental equations :

$$U/X = D\zeta/4\pi\eta \text{ (electrophoresis)} \quad . \quad . \quad . \quad . \quad (1)$$

$$V/J = E/P = D\zeta/4\pi\eta\kappa \text{ (electrosmosis and stream potential)} \quad . \quad (2)$$

(U is the electrophoretic velocity under potential gradient X, V the volume of liquid electrosmotically transported per second by a current J, and E the stream potential set up by a pressure difference P; D, η, and κ are respectively the dielectric constant, viscosity, and specific resistance of the liquid). Subject to certain restrictions, Smoluchowski's theory indicates that equation (1) is applicable to the electrophoresis of suspended particles of any shape, and also to the electrosmotic velocity of a liquid in the neighbourhood of a surface to which the applied field is tangential, and that equation (2) is applicable both to capillary tubes and to porous diaphragms. The necessary restrictions are given by Smoluchowski, and have been

[18] F. Powis, *Z. physikal. Chem.*, 1915, **89**, 186.

[19] H. Freundlich and G. V. Slottman, *ibid.*, 1927, **129**, 305; H. Mueller, *Kolloidchem. Beih.*, 1928, **26**, 257; P. Tuorila, *ibid.*, 1928, **27**, 44; A. March, *Kolloid-Z.*, 1928, **45**, 97; J. N. Mukherjee and S. P. Rai-Choudhuri, *Nature*, 1928, **122**, 960; S. Mattson, *Soil Science*, 1929, **28**, 373; D. R. Briggs, *J. Physical Chem.*, 1930, **34**, 1326; S. W. Pennycuick, *J.*, 1930, 1447; H. R. Kruyt, A. C. W. Roodvoets, and P. C. van der Willigen, *Colloid Symposium Monograph*, 1926, 304; H. R. Kruyt and D. R. Briggs, *Proc. Acad. Sci. Amsterdam*, 1929, **32**, 384; H. R. Kruyt and E. F. de Haan, *Kolloid-Z.*, 1930, **51**, 61.

[20] See ref. (75).

discussed in detail by M. Mooney,[21] D. C. Henry,[22] and E. Manegold and K. Solf.[23] Following the suggestion of M. Gouy,[24] the " outer sheet " of the double layer is nowadays considered to be, not a laminar distribution of electrification, but a diffuse ionic " atmosphere," producing a continuous rather than a sudden fall of potential from the rigid phase into the liquid. It is not agreed whether Smoluchowski's theoretical deduction is applicable to a double layer of this type. P. Debye and E. Hückel [25] and E. Hückel [26] consider it is not, and replace equation (1) by

$$U/X = CD\zeta/\eta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where C is a constant depending on the shape of the particle, and having the value $1/6\pi$ for a sphere. On the other hand, Mooney and Henry have both shown that Debye and Hückel's conclusions rest on a particular assumption, not generally realised in practice, about the distribution of the applied electric field, and Henry claims to have shown that for electrically insulating particles of spherical or cylindrical form and of sufficiently large size, equation (1) holds. Debye and Hückel's conclusion that the electrophoretic velocity of a particle should depend on its shape is supported by D. A. Newton,[27] K. van der Grinten,[28] and B. W. Currie ;[29] the first two authors quoted, however, assume that the surfaces of broken particles of a given material will have the same ζ-potential as surfaces prepared by fusion or polishing, an assumption which H. Abramson [30] and D. C. Henry [31] claim to be erroneous. By making use of the discovery previously referred to, *viz.*, that particles of glass, quartz, and many other materials adsorb a layer of protein from dilute solution and behave electrokinetically as protein, H. Abramson [32] has shown most conclusively that the electrophoretic velocity of a relatively large particle does not depend on its shape, and that equation (1) is generally valid in such cases. This is confirmed for wax suspensions by D. C. Henry [33] and for a macroscopic cylindrical surface by C. G. Sumner and D. C. Henry.[34]

Equation (1) strictly applies to the motion of a single particle in

[21] *J. Physical Chem.*, 1931, **35**, 331 ; *A.*, 429.
[22] *Proc. Roy. Soc.*, 1931, [*A*], **135**, 106 ; *A.*, 1232.
[23] *Kolloid-Z.*, 1931, **55**, 273 ; *A.*, 905.
[24] *Compt. rend.*, 1909, **149**, 645 ; *J. Physique*, 1910, **9**, 457 ; see also O. Stern, *Z. Elektrochem.*, 1924, **30**, 508.
[25] *Physikal. Z.*, 1924, **25**, 49. [26] *Ibid.*, p. 204.
[27] *Phil. Mag.*, 1930, [vii], **9**, 769 ; *A.*, 1930, 858.
[28] *Compt. rend.*, 1924, **178**, 2083 ; *A.*, 1924, ii, 664.
[29] *Phil. Mag.*, 1931, [vii], **12**, 429 ; *A.*, 1122.
[30] *J. Physical Chem.*, 1931, **35**, 289 ; *A.*, 429.
[31] Ref. (22). [32] Ref. (30). [33] Ref. (22).
[34] *Proc. Roy. Soc.*, 1931, [*A*], **135**, 130 ; *A.*, 1232.

an infinite liquid; a correction to take account of the hydrodynamical interaction of a multiplicity of particles has recently been published.[35]

Some doubt has now been thrown on the validity of the Helmholtz–Smoluchowski equations from a different direction. N. Thon[36] points out that for the electrophoresis of a variety of solid particles in the presence of electrolytes, the maximum of the ζ–c curve, when it occurs, is found at a concentration in the neighbourhood of 1 millimol. per litre, and similarly minima occur at about 3 millimols. per litre. On the other hand, in stream-potential measurements with glass capillaries, the maxima and minima occur at concentrations roughly a thousand times smaller. This is taken to indicate that the "ζ" as evaluated by electrophoresis is not the same as that arrived at by stream-potential measurements. G. Ettisch and A. Zwanzig[37] find that although ζ (by stream potential) is independent of the applied pressure in aqueous solutions, this is far from being true in aqueous methyl alcohol, and conclude that ζ is not a constant independent of the experimental method and conditions employed. E. Manegold and K. Solf[38] find similarly that the electrosmotic transport through a membrane filter is not proportional to the current, as required by equation (2), but that V/J diminishes with increasing J. They attribute this behaviour to alterations in the effective viscosity, specific conductivity, and dimensions of the electrical double layer, and propound a quantitative theory to take account of these factors. It is evident that direct comparisons of the principal electrokinetic methods are urgently required; in the only recent investigation of this type,[39] a comparison of the electrophoretic and stream-potential methods applied to surfaces covered with the same protein indicates that the two methods do actually lead to the same value of ζ, but this needs confirmation over a wider field.

PART III.—COLLOID CHEMISTRY OF CLAYS.

By R. K. SCHOFIELD.

Base Exchange.—The discovery of the phenomenon of base exchange is due to J. T. Way, who found that soil has the power of removing small quantities of dissolved base, such as ammonia or

[35] W. O. Kermack, A. G. McKendrick, and E. Ponder, *Proc. Roy. Soc. Edin.*, 1929, **49**, 170; *A.*, 1929, 878.

[36] *Z. physikal. Chem.*, 1930, **147**, 147; *A.*, 1930, 696.

[37] Ref. (6).

[38] Ref. (23).

[39] H. A. Abramson and E. B. Grossman, *J. Gen. Physiol.*, 1931, **14**, 563.

lime, from the solution. He also observed that when a solution of a salt, such as potassium sulphate, percolates through a soil, some of the potassium sulphate is removed and an equivalent quantity of calcium sulphate appears in the solution. He explained this phenomenon by supposing an amount of lime, which had previously been taken up by the soil, had exchanged with potash; hence the term " base exchange." In the light of the electrolytic dissociation theory, the phenomenon might be called kationic exchange, as it is evident that it is sufficient to suppose that kations only are involved; nevertheless, the older word is still usually employed.

The phenomenon is of great importance in agriculture, as it provides a mechanism by which plant nutrients, which would otherwise be readily washed out of the soil, are retained for the use of succeeding crops. The buffer action involved in the phenomenon also stabilises the p_H in the soil, thereby rendering it more equitable as a medium for plant life. A right understanding of the phenomenon is proving to be of increasing service in the ceramic industry, for important changes are brought about in the physical properties of clays as a result of quite small changes in the proportions of the exchangeable kations. Base exchange is the basis of the " permutit " water-softening process, which relies on the fact that when present in equal concentrations, calcium ions are taken up by the permutit in preference to sodium. Apart altogether from these practical applications, the study of this subject has an important bearing on general colloidal theory, and it is this aspect which is chiefly emphasised in the following paragraphs.

Before discussing in detail the colloid chemistry of clay, it is necessary to make clear exactly what materials may be considered as falling into this category. To the agriculturist, clay consists of the finely divided mineral constituents of a soil. Originally the division was fixed with respect to a convenient time of settling through water, but it was later found that the particles which settled through water faster than about 1 cm. an hour usually showed little base exchange activity. This imposes an upper limit to the particle size of about 2 μ. In the discussion that follows the above definition is implied. To the ceramist, the word " clay " means rather a material consisting of small laminated particles having the firing properties required for pottery work. For this purpose, a material is used containing particles larger than those recognised as agricultural clay, but here again these particles do not contribute appreciably to the base exchange capacity of the material.

When clay is washed with dilute acid, an exchange occurs between the hydrogen ions and other kations which had previously been

held by the clay. The material thus produced is generally spoken of as a hydrogen clay, or, sometimes, as an acid clay. The reason for specifying that the acid should be dilute is that in strong acid, particularly when hot, kations come into solution as a result of the decomposition of the clay particles. In support of the view that no important decomposition occurs with dilute acid may be cited the experiments of W. P. Kelley and S. M. Brown,[1] S. Mattson,[2] and B. D. Wilson,[3] which show that the same quantities of exchangeable base are removed by $N/20$-hydrochloric acid as by N-ammonium chloride or by electrodialysis of the clay. At the same time, it was found that the dilute acid removed small quantities of silica and sesquioxides—rather more than the electrodialysis—while practically none was removed by N-ammonium chloride. Even with dilute acid, the amount (reckoned in equivalents) is only a few units % of the exchangeable bases.

The view that hydrogen clay is a colloidal acid has been supported by a number of lines of evidence. F. E. Rice and S. Osugi[4] studied the rate of inversion of cane sugar in soil suspensions. They showed that inversion only took place in the presence of the soil, not in the water extract, and, further, that its rate was proportional to the quantity of the soil used. They interpreted this inversion as being caused by the acidity of the soil, stating that these soil acids are not soluble in water and therefore cannot be removed by water extraction. R. M. Salter and M. F. Morgan[5] confirmed the result that the acidity of an acid soil suspension increases with the concentration of the soil as measured by the rate of inversion of sucrose, and also by the hydrogen electrode, but they showed that the proportionality between the hydrogen-ion concentration and the soil concentration only held over a limited range. R. Bradfield,[6] using electrodialysed colloidal clays, compared the variation of the p_H of the clay concentration with that obtained on dilution of acetic acid, and argued from the similarity of the two curves that the clay should be regarded as a weak colloidal acid. This point has been investigated in great detail by G. Wiegner and H. Pallmann[7] in a series of papers, who showed quite generally for an acid colloidal system that an electrode can be affected by hydrogen ions

[1] *Univ. of Calif. Agric. Expt. Station of Coll. of Agric.*, 1924, Tech. Paper, No. 15.

[2] *J. Agric. Res.*, 1926, **33**, 553.

[3] *Soil Sci.*, 1928, **26**, 407.

[4] *Ibid.*, 1918, **5**, 333.

[5] *J. Physical Chem.*, 1923, **27**, 117.

[6] *Ibid.*, 1924, **28**, 170.

[7] *Verhdl. II. Komm. Intern. Bodenkunde Gesell. Budapest*, Teil B., 1929, 92; *Z. Pflanz. Düng.*, 1930, [*A*], **16**, 1; *Ergeb. Agrik.-chem.*, II, 1—37; G. Wiegner, *Kolloid-Z.*, 1930, **51**, 49; *J. Soc. Chem. Ind.*, 1931, **50**, 103T; H. Pallmann, *Kolloidchem. Beih.*, 1930, **30**, 334.

dissociated from the colloidal particle, so that, if a hydrogen clay is dispersed in pure water, the acidity increases as the concentration of the clay increases, and, in fact, the increase in hydrogen-ion concentration is proportional to the concentration of the colloidal sol provided the clay concentration be not too large. Further, if a salt such as sodium chloride is added to the clay, the dispersion medium becomes more acid, but the acidity of the clay is decreased, that is, the effect of increasing the concentration of the clay on the hydrogen-ion concentration of the sol was decreased. They showed these results were not mere electrode effects by checking the potentiometer measurements of the hydrogen-ion concentration against measurements on the rate of inversion of cane sugar; and further, that for a deflocculated colloidal system both methods gave almost exactly the same value for the hydrogen-ion concentration, while for a flocculated system the sugar inversion gave a higher value than the potentiometric, which was interpreted as due to the sugar molecules being able to get inside the loose floccules and to be inverted there, while the electrode was unaffected by these locked-up hydrogen ions. These experiments provide strong evidence that the particles of an acid clay are surrounded by a swarm of hydrogen ions which can be displaced by other kations. The clay shows all the properties of a true colloidal acid, as described, *e.g.*, by L. Michaelis.[8]

A suspension of hydrogen clay may be titrated potentiometrically against an alkali by using a hydrogen electrode or, in the lower p_H range, a quinhydrone electrode, and the curve so obtained bears at least a superficial resemblance to that for a weak acid. Those workers who have been reluctant to accept the colloidal acid theory have stressed the fact, first ascertained by Bradfield, that the position of the titration curve with sodium hydroxide differs considerably from that obtained with baryta. It might be urged that this difference, although somewhat larger than that obtained with, say, phosphoric acid, is, nevertheless, of the same nature. A striking fact was later pointed out by H. B. Oakley,[9] *viz.*, that if titrations are carried out in the presence of an $N/2$-solution of the chloride of the same metal, the curves for the different alkalis are all superimposed, provided the p_H do not exceed 9. In other words, the clay will take up a definite amount of base and reach a definite p_H for a given addition of hydroxide when the added kation is sodium, potassium, calcium, or barium. Although Oakley did not emphasise the fact, this result is in reality very singular. For, in the case of simple weak acids,

[8] *Colloid Symposium Monograph*, 1925, **2**, 1; "The Effect of Ions in Colloidal Systems," Williams & Wilkins Co., Baltimore.

[9] *J.*, 1927, 2819.

the titration curves with different bases become more nearly coincident the weaker the solutions, and become increasingly more divergent with the addition of neutral salts, whereas the reverse is true of clays. Nevertheless, there is no doubt about the fact, of which use is made in the measurement of soil acidity. In the case of an aqueous soil suspension the p_H varies considerably according to the season, being influenced by the concentration of salts in the soil solution. The addition of potassium chloride to the solution reduces the p_H, and gives a value which is much more stable and practically uninfluenced by seasonal conditions.

The instability of a clay particle in a medium of p_H greater than 9 has made it difficult to decide whether or not there is a definite number of equivalents of exchangeable hydrogen associated with a given weight of clay. At high p_H's in the presence of the alkali kations soluble aluminates and silicates are formed, while with the alkaline-earth kations it is probable that aluminates and silicates are still formed, but, being insoluble, form a layer over the clay particles. Both the method of R. Bradfield,[10] in which hydrogen clay is added to a strong base, and also that of D. J. Hissink,[11] in which a soil is placed in excess baryta, and the amount not taken up determined either by simple or conductimetric titration, are open to objection on this ground. The difficulty in finding an end-point in the titration of a hydrogen clay with an alkali has led some workers to advocate the theory that the process involved is one of adsorption in which both the hydroxyl ions and the kations are taken up. In support of this view, S. Mattson [12] quotes an experiment showing that when a hydrogen clay is treated with calcium hydroxide, the gain in weight of the oven-dried clay corresponds to an adsorption of calcium hydroxide and not to a replacement of hydrogen ions by calcium ions. Such an experiment cannot, however, be regarded as having any direct bearing on the question as to whether or not a hydrogen clay in water is a colloidal acid. Whether or not the dried clay is an anhydride of the acid, and whether the dried calcium clay is a hydrate, are obviously irrelevant to the point at issue. The problem is very similar to that of deciding whether carbonic acid exists in solution or whether the bicarbonate ion is formed by a direct union of the hydroxyl ion with carbon dioxide.

Permutits.—A considerable proportion of the work that has been carried out on base exchange in permutits was published before many of the properties of the hydrogen clay outlined above came to

[10] *J. Amer. Chem. Soc.*, 1923, **45**, 2669.
[11] *Z. Pflanz. Düng.*, 1925, [*A*], **4**, 137.
[12] *Soil Sci.*, 1928, **25**, 289.

light. At this time it was also supposed that the laws governing base exchange in permutits could be applied directly to clays. While there is undoubtedly a great similarity between the behaviour of permutits and zeolites on the one hand, and clays on the other, important differences nevertheless exist. As instances of such differences may be cited the difference in speed at which equilibrium is reached in the two systems. J. T. Way initially showed that for clays this is attained almost instantaneously, while with permutits it may take many hours. G. Wiegner[13] has interpreted this result as showing that, whereas base exchange in clays is an external surface phenomenon, that in permutits takes place inside fine capillaries. This idea is supported by the fact that a large kation, such as methylene-blue, can quantitatively displace all the exchangeable base from a clay, but is not taken up appreciably by a permutit. In the case of zeolites, it is usually considered that the exchangeable ions occupy positions in the crystal lattice itself, and that exchange in this case occurs by a movement of the ions through the crystal.

Various attempts have been made to formulate quantitative laws connecting the equilibrium concentration of ions in the solution with those held by the permutit. It has been found that, using a permutit containing only one kind of kation and a chloride of the alkali and the alkaline-earth metals, the amount of exchange depends only on the total amount of permutit and salt present, and not on the actual concentration of the salt, that is, the exchange is independent of the amount of water present.[14] As to the relation between the amount of salt added and the amount of kations exchanged, two distinct methods of attack have been used: the empirical method, which uses Freundlich's adsorption isotherm, and a semi-theoretical method, which employs the law of mass action to give some kind of theoretical justification to the formula proposed. The Freundlich isotherm gives a tolerably accurate representation of the effect of the quantity of added salt on the total exchange taking place.[15] The Freundlich equation states that, if the quantity of permutit, or clay, remains constant

$$(a - c) = kc^{1/p},$$

where a is the initial concentration of the added kation, c its

[13] *J. Soc. Chem. Ind.*, 1931, **50**, 65T.

[14] R. Ganssen, *Jahrb. der Kgl. preuss. geolog. Landesanst. u. Bergakad.*, 1905, **26**, 179; **27**, 63; V. Rothmund and G. Kornfeld, *Z. anorg. Chem.*, 1918, **103**, 129; **108**, 215; G. Wiegner and K. W. Müller, *Z. Pflanz. Düng.*, 1929, [*A*], **14**, 321.

[15] G. Wiegner and H. Jenny, *Kolloid-Z.*, 1927, **42**, 268; G. Wiegner, *J. Landw.*, 1912, **60**, 111, 192; H. Jenny, *Kolloidchem. Beih.*, 1927, **23**, 428.

equilibrium concentration, and k and $1/p$ are constants. This equation can be rewritten as

$$x = k'[c/(a - c)]^{1/p'} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where x is the amount of the added kation adsorbed by the substrate and in this form is seen to be independent of the actual concentrations. It suffers from the weakness that it allows of no upper limit for x, which must in reality exist. But over the range of concentrations usually employed it gives a very fair representation of the exchange.

The second method, based on the law of mass action, has been developed in two forms. The first,[16] developed by V. Rothmund and (Frl.) G. Kornfeld and based on the ordinary mass-action law in solution, is

$$\frac{[B_1]\ \text{clay}}{[B_2]\ \text{clay}} = K\left(\frac{[B_1]\ \text{solution}}{[B_2]\ \text{solution}}\right)^n$$

where $[B_1]$ is the concentration of kation 1, $[B_2]$ that of kation 2, and [ ] solution refers to the concentration of the kation in the solution, while [ ] clay refers to the amount of the kation adsorbed per g. of clay, and K and n are constants. Anderegg and Lutz, and independently Kerr, claimed that for soils $n = 1$ if $[B_1]$ and $[B_2]$ have the same valency, but Kerr claims to have shown that if $[B_1]$ and $[B_2]$ have different valencies the formula should be

$$\frac{[B_1]^2\ \text{clay}}{[B_2]\ \ \text{clay}} = K\left(\frac{[B_1]^2\ \text{solution}}{[B_2]\ \ \text{solution}}\right)$$

where $[B_1]$ is a univalent and $[B_2]$ a bivalent kation, and from this result concludes that clay behaves as a monobasic acid. This formula is not independent of concentration, so appears to be in contradiction to Wiegner and Müller's results for permutits, in which they showed that, even if the valencies of the two kations differ, their equilibrium distribution is independent of the actual amount of water present. This contradiction needs further investigation.

The second form developed by Langmuir for adsorption at an interface, and independently by P. W. E. Vageler [17] as an empirical equation, is

$$y = Sx/(C + x)$$

where y is the quantity of the base adsorbed, and x the amount of the base in equilibrium with the substrate (Vageler first assumed x

[16] R. Gans, *Centr. Min.*, 1913, 699, 728; V. Rothmund and G. Kornfeld, Ref. (14); F. O. Anderegg and R. P. Lutz, *Soil Sci.*, 1927, **24**, 403; H. W. Kerr, *J. Amer. Soc. Agron.*, 1928, **20**, 309; *Soil Sci.*, 1928, **26**, 385.

[17] *Landbouw.* (*Java*), 1928, No. 5, 244; P. W. E. Vageler and J. Woltersdorf, *Z. Pflanz. Düng.*, 1930, [*A*], **15**, 329.

was the amount of base added), S is the maximum exchange capacity for the substrate, and C is a constant. No critical comparative studies on the relative efficiencies of these three equations have been made.

A comparison of the replacing power of different kations has been worked out in considerable detail for permutits,[18] but not so extensively for clays.[19] For a clay, or permutit, saturated with a given base, the lithium kation is the weakest replacer of the adsorbed base, and sodium, potassium, rubidium, and cæsium follow in order; finally comes hydrogen, which is the strongest replacer. For permutits, and probably for clays, though this point has not been properly confirmed, a given concentration of a definite kation can displace more lithium from a lithium permutit than sodium from an equivalent amount of sodium permutit, and so on. For the alkaline earths, magnesium is the weakest replacer, followed in order by calcium, strontium, and barium; but, unlike the case of the alkali metals, a given concentration of a definite kation displaces more barium than calcium and more calcium than magnesium. This result holds for both clays and permutits. The explanation offered by Wiegner and Jenny for this anomaly is that the ions are held to the permutit by hydroxyl bindings, and, since magnesium hydroxide is more insoluble than calcium hydroxide, the magnesium is assumed to be more tightly bound to the permutit surface than is the calcium. Similarly, for strontium and barium.

Wiegner and Jenny, working with permutits, expressed their experimental results by fitting to them equations of the form (1). They found that $1/p'$ depended mainly on the valency of the adsorbed and added kations, and the constant of proportionality depended both on the kation initially present in the permutit and on the exchanging kation. For a permutit containing a given base, k' was smallest when lithium was the added kation, and increased steadily to cæsium for the alkali kations, and was smallest when magnesium and largest when barium was the added kation for the alkaline-earth kations. Further, the constant k' appeared to be proportional to the true ionic volume of the ion, *i.e.*, its volume deduced from X-ray crystallographic data. Wiegner and Jenny interpreted these results on the ionic hydration theory, namely, that for an ion of a given valency the smaller its radius the more strongly it is hydrated, and therefore the larger its effective volume. Thus, the lithium ion, being heavily hydrated, is effectively larger than the cæsium ion. As further evidence in favour of the hydration hypothesis it was shown[20] that, if the base exchange was carried out

[18] H. Jenny, ref. (15); G. Wiegner and H. Jenny, ref. (15).
[19] K. K. Gedroiz, *J. Exp. Agron.* (*Russ.*), 1918, **19**, 269; **20**, 31.
[20] Wiegner and Jenny, ref. (15).

in alcoholic solution, not only was the amount of exchange increased, but the relative order of the ions was altered, and, in fact, in an 80% alcoholic solution potassium was more strongly adsorbed than was cæsium or sodium, which are equally strongly adsorbed, so that, as the alkali ions become dehydrated the relative difference in replacing power between them becomes more nearly equal. Wiegner and Müller [21] tried to see how far a simple reduction of the dielectric constant of the dispersion medium would explain the increased exchange due to dehydration, and investigated the effect on the exchange of two sugars, *viz.*, glucose, which reduced the dielectric constant of the water very considerably, and cane sugar, which affected it but little. They found that neither sugar had any appreciable effect, and explained this by assuming that the surfaces on which base exchange takes place in a permutit are situated in pores, whose size is such that sugar molecules are too large to enter, but alcohol molecules are small enough to do so. In confirmation of this explanation, Wiegner [13] has shown that tri- and tetra-methyl-ammonium ions are barely adsorbed by permutits, whilst even the monomethylammonium ions are adsorbed less strongly than the ammonium. Thus the pore size in permutits seems to be such as to allow alcohol and ammonium ions and even, to a certain extent, monomethylammonium ions to enter, but to be too fine to give access to larger ions.

In considering the external influences which might affect base exchange, Wiegner [15] studied the effect of temperature and found that it exerted no appreciable influence between 0° and 50°. The effect of the anions has been studied by A. Baumann and U. Gully,[22] E. Ungerer,[23] and A. N. Puri,[24] whose results bear out the view that the anions influence the phenomenon only in so far as they affect the activity of the kations and the hydrogen-ion concentration.

Flocculation Phenomena.—When soil is shaken with about 100 times its weight of dilute (say 0·1%) sodium carbonate solution, the suspension does not clear if allowed to stand for weeks or even for years. It is only necessary to add a small quantity of acid (slightly more than sufficient to neutralise the carbonate) to cause all the suspended material to settle, leaving a clear supernatant liquid. The first condition is usually spoken of as deflocculated : the second as flocculated. In the deflocculated condition the soil particles are separately dispersed, and the smallest of them can be seen under the ultramicroscope to execute Brownian movement. To obtain the size distribution curve by observation of the rate of settling, a

[21] Ref. (14). [22] *Mitt. kgl. bayr. Moorkulturanstalt*, 1910, **4**, 39.
[23] *Z. Pflanz. Düng.*, 1930, [*A*], **18**, 342.
[24] *Mem. Dept. Agric. India*, 1930, **11**, 1.

soil is always brought into the deflocculated condition by the addition of ammonia, sodium carbonate, or sodium hydroxide according to the method employed. P. Tuorila [25] has followed the transition from the flocculated to the deflocculated condition in the case of clay suspensions, about 0·1% by weight, which are sufficiently dilute to be studied in the ultramicroscope. The suspensions used were approximately monodisperse, *i.e.*, all the suspended particles were of approximately the same size. When more than a critical amount of flocculant has been added to such a system, coagulation proceeds at a rate which follows the Smoluchowski equation for rapid coagulation, *i.e.*, the rate of decrease of the particle numbers depends only on the initial number of particles present in unit volume, and is not increased by further additions of the flocculant or influenced by its nature, provided that it be either a neutral salt or a dilute acid. The conclusion to be drawn from this result is that, under rapid coagulation, the encounters between the clay particles are brought about solely, or at any rate mainly, by their Brownian movement, and that two particles once having come together remain together. When less than the critical amount of flocculant has been added, coagulation proceeds at a slower rate, but does not in general follow the Smoluchowski equation for slow coagulation, which supposes that only a certain constant fraction of the encounters of the particles leads to their adhering, the fraction increasing with the amount of flocculant added. According to this equation, the reciprocal of the particle numbers should increase linearly with the time. Tuorila showed that, with a clay suspension, the rate of increase of $1/N$ falls off with the time, *i.e.*, the particle numbers do not diminish as rapidly as one would expect from the Smoluchowski theory. Tuorila was inclined to attribute this discrepancy to a lack of uniformity in the size of the clay particles, resulting in a variation of the electrokinetic potentials. An alternative explanation is that the secondary particles do not remain stable under collision, as assumed by Smoluchowski, but that there is a certain probability of their partial break up. This suggestion is made more plausible by the fact that a flocculated clay suspension is readily redispersed if sufficiently diluted.

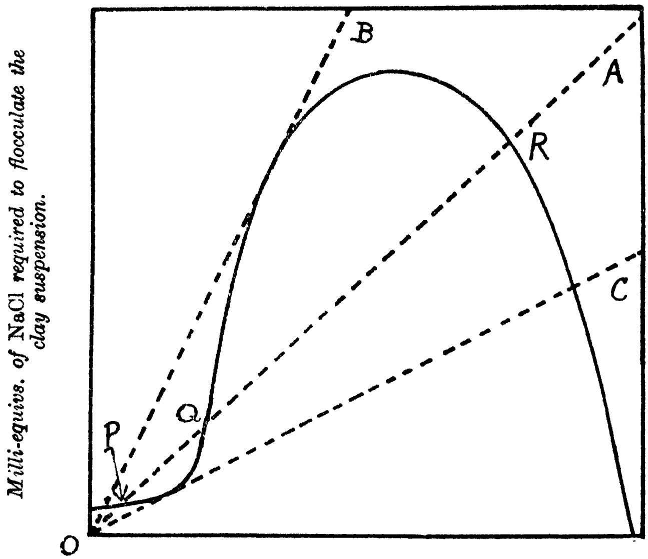
A further case has been investigated by Wiegner [26] and Tuorila [27] in which collisions between particles are brought about by sedimentation of some particles relative to others in the suspension. Provided a sufficient electrolyte concentration be present, they showed that this mechanism was sufficient to account for the decrease in particle numbers in such a system. Much of the earlier work on

[25] *Kolloidchem. Beih.*, 1928, **27**, 44. [26] *Z. Pflanz. Düng.*, 1928, [*A*], **11**, 1 5.
[27] *Kolloidchem. Beih.*, 1927, **24**, 1.

the flocculation of soil suspensions has been complicated by the fact that these two mechanisms have not been separated.

The majority of agricultural clays, when freed from soluble electrolytes, are readily dispersed in water and remain deflocculant. Several workers have determined the quantity of a neutral salt which must be added to produce a recognisable stage of flocculation. Much of the earlier work gave conflicting results because insufficient account was taken of the influence of the exchangeable base in the clay. This point is illustrated by the curve (Fig. 4), which gives

Fig. 4.



Milli-equivs. of NaOH *added to the hydrogen clay.*

the concentration of sodium chloride required to produce a definite degree of flocculation in clays containing increasing amounts of exchangeable sodium, these clays being prepared by adding increasing amounts of sodium hydroxide to hydrogen clay. Measurements of this kind have been made by R. Bradfield,[28] and A. F. Joseph and H. B. Oakley.[29] The sigmoid shape of the curve accounts for the " anomalous flocculation " discovered by Oakley,[30] for, on the addition to a hydrogen clay of a mixture of sodium chloride and sodium hydroxide, corresponding to the straight line *OA* on the diagram, flocculation first occurs at *P*, deflocculation at *Q*, and the clay again flocculates at *R*. It is evident that only mixtures repre-

[28] *J. Amer. Soc. Agron.*, 1925, **17**, 253. [29] *Nature*, 1926, **117**, 624.
[30] *Ibid.*, **118**, 661.

sented by lines falling between *OB* and *OC* will give rise to this phenomenon. In discussing the flocculating action of neutral salts, it is important to distinguish cases, such as the above, in which the kation of the salt is the same as that combined with the clay, and the more general one where this is not the case and where the conditions will be complicated by base exchange. In the special case where a neutral salt is added to a hydrogen clay, the complication from this cause is not very great, since unless an alkali or a salt of a weak acid is present, little of the hydrogen will exchange with the added kation. K. K. Gedroiz [31] showed that the flocculating power of kations increases with their valency, which is in accordance with the Hardy–Schulze valency rule. Tuorila [32] gives evidence to show that the rate of coagulation is closely connected with the electrokinetic potential as determined by their cataphoretic mobility. The results are the same for the kations in a given valency class, but are found to depend somewhat on the valency.

M. S. Anderson,[33] S. Mattson,[34] and L. D. Baver [35] have shown that suspensions of clays containing a bivalent alkaline-earth kation (magnesium, calcium, strontium, barium) are less stable and have a lower electrokinetic potential in the absence of electrolytes than clays containing a univalent alkali kation (lithium, sodium, potassium) or hydrogen, as is shown in Table I. As may be seen,

TABLE I.

Mean electrokinetic potential of clays relative to the calcium clay.

	Anderson.	Mattson.	Baver.
Ca-clay	100	100	100
Mg-clay	99	—	110
K-clay	134	—	164
Na-clay	149	191	169
H-clay	23	168	128

Anderson found that a hydrogen clay has a lower electrokinetic potential than the corresponding calcium clay, but this result has not been confirmed by other workers. Mattson, however, made the interesting observation that electrolytes depress the electrokinetic potential of a hydrogen clay much more rapidly than a calcium clay, and, in fact, it does not require a large electrolyte concentration to give the hydrogen clay a lower electrokinetic potential than the calcium clay. If clays containing an alkali kation are considered, the more hydrated the kation, or the lower its atomic

[31] Bureau of Agric. and Soil Sci., Scientific Communications of Dept. of Land Organisation and Agric., Petrograd, 1915, Comm. No. 24. (Used only in the English translation issued by U.S. Dept. of Agric., 1923.)

[32] *Kolloidchem. Beih.*, 1928, **27**, 44.

[33] *J. Agric. Res.*, 1929, **38**, 565. [34] *Soil Sci.*, 1929, **28**, 373.

[35] *Missouri Expt. Sta. Res. Bull.* No. 129, 1929.

weight, the higher is the electrokinetic potential of the pure clay suspension, and the more stable it is. Mattson further showed that if the theory of the critical potential is valid for clay suspensions, then this potential depends on the exchangeable ion present. For instance, he calculated a critical potential of − 55 millivolts for a sodium clay, whereas that for the corresponding calcium clay was only − 22 millivolts.

These results throw much light on an apparent anomaly in the behaviour of many colloidal suspensions. In general, if an electrolyte is added to an electronegative sol its electrokinetic potential is depressed, unless the electrolyte is a sodium or potassium salt, in which case it often rises a little before falling. Mattson, for example, found that if potassium chloride is added to a calcium clay suspension, the electrokinetic potential first rises a little before falling, but if it is added to a sodium clay suspension the electrokinetic potential falls continuously. This anomaly is probably due to secondary effects consequent upon base exchange.

When potassium chloride is added to a calcium clay suspension, a certain amount of calcium will be exchanged for potassium, giving a clay containing both adsorbed calcium and adsorbed potassium. The introduction of potassium into this system raises its electrokinetic potential, and if this rise more than counterbalances the depressing effect of the added electrolyte, the electrokinetic potential of the clay particles rises. But if the clay is a sodium clay, the exchange of potassium into the complex with sodium will depress the electrokinetic potential of the clay particles, so both effects reduce the potential.

Anderson and Mattson [36] showed that the higher the ratio of silica to sesquioxides in a clay, or the higher its exchange capacity, the higher is the electrokinetic potential of the clay suspension when containing a given kation, in the absence of added electrolyte, and the more stable is this suspension. Mattson [34] considered that this effect pointed to a greater hydration of a clay with the high exchange capacity. He showed that if clays were dehydrated by using 75% alcohol as the dispersion medium, the concentration of added electrolyte is more nearly the same for different clays, as Table II, taken from his paper, shows.

The exchange capacity for Sharkey and for Norfolk clay is respectively 0·796 and 0·207 milli-equiv. per g.

In general, when a very dilute clay suspension coagulates it never clears completely unless centrifuged, and the complex particles are either not visible or barely visible to the naked eye. A characteristic of the coagulation of clay suspensions in alkaline media is

[36] *U.S. Dept. of Agric. Bull.* No. 1452, 1926.

that large loose aggregates, or flocs, are formed, which settle rapidly, leaving a clear dispersion medium, and that this flocculation is several times more rapid than the usual rapid coagulation in a neutral medium. Thus, Brownian movement cannot be the only agent bringing about encounters between the particles. The early investigators who studied this effect explicitly, *e.g.*, N. M. Comber,[37] Mattson,[38] and F. Hardy,[39] only studied the effect in the presence of calcium salts, but it was not until Tuorila [40] investigated the influence of other kations that a critical discussion of this effect could be undertaken. He showed that the possibility of the formation of a weakly soluble salt was an essential part of the phenomenon.

TABLE II.

Concentration of electrolyte required to coagulate a clay suspension in aqueous and in alcoholic solution.

Dispersion medium.	Clay.	NaCl coagulating an Na-clay.	KCl coagulating a K-clay.
Water	Sharkey	0·08	0·03
	Norfolk	0·004	0·003
75% Alcohol	Sharkey	0·001	0·0005
	Norfolk	0·001	0·0003

Tuorila showed that if sodium hydroxide is added to a clay suspension containing the chloride of a bivalent metal in solution, the more insoluble the hydroxide of this metal the lower is the concentration of the chloride required to bring about this abnormally rapid flocculation. He further showed that, whenever this flocculation takes place, the conditions are such that if any colloidal particles of the hydroxide were formed in the suspension they would be electropositive and, therefore, of opposite charge to the clay particles. If such a hydroxide suspension is mixed with a clay suspension an extremely rapid and analogous flocculation sets in. The course of this flocculation was followed under the ultramicroscope, and it was shown that the rate of decrease of particle numbers is much greater than is given by the Smoluchowski theory for rapid coagulation of monodisperse systems of spherical particles. The quantity A/ρ, the ratio of the attractional radius of a particle to its hydrodynamical radius, was as high as 70 after coagulation had been proceeding for 90 seconds, had fallen to 20 after 6 minutes, and after 2 hours had only fallen to 4, while for the same clay suspension coagulating in a neutral medium A/ρ was about 2, so collisions between particles are evidently caused, not only by their Brownian motion, but also by the attractional forces between them.

[37] *J. Agric. Sci.*, 1920, **10**, 425; 1921, **11**, 450; 1922, **12**, 372.
[38] *Kolloidchem. Beih.*, 1922, **14**, 227.
[39] *J. Physical Chem.*, 1926, **30**, 254.
[40] Ref. (25).

R. K. Schofield and G. W. Scott Blair [41] have measured the depth of the sediment of flocculated clay thrown down from suspensions of clay containing different exchangeable ions by varying the amounts of the corresponding chlorides, and have also made relative measurements of the strength of the rigid structure of the sediments. They found that the substitution of calcium for some of the exchangeable hydrogen does not affect the sediment volume, nor is this influenced by the concentration of calcium chloride and barium chloride until these reach normality of about $N = 1$. When the clay contains exchangeable sodium or potassium ions, high concentrations of the corresponding chlorides are required to flocculate the clay. In these cases, and whenever the clay is suspended in a chloride of about N-concentration or above, a thixotropic gel of larger volume is formed. The strength of the rigid structure of the sediment depends on the exchangeable ions present and on the nature and concentration of the added salt. The relationships involved appear to be complex. The reproducibility of the sediment volume obtained in dilute salt solutions suggests that a measurement of this quantity may be of use in soil studies.

The distinction between a flocculated and a deflocculated clay suspension persists even when the suspension is relatively concentrated. Just as the condition of many colloids in suspensions is judged by their viscosity, so observations on the flow properties of clay suspensions may be used in studying this distinction. The problem is, however, complicated by the fact that clay suspensions do not obey Poiseuille's law, except at great dilution, and consequently the flow properties of the more concentrated pastes cannot be represented by a single constant. R. E. Wilson and F. P. Hall,[42] following E. C. Bingham,[43] showed that the graph connecting the rate of flow and applied pressure is linear except for low pressures but that the linear portion when extrapolated does not pass through the origin but makes a positive intercept on the pressure axis. The flow at high pressures can therefore be expressed by two constants, one representing a stress and measured by the intercept, and the other analogous to viscosity which can be calculated from the slope (sometimes termed pseudo-viscosity). M. Simonis,[44] and later, W. L. Shearer [45] and others, studied the influence of flocculants and deflocculants on these properties. In general, a paste shows a higher intercept and a higher pseudo-viscosity when flocculated

[41] *Trans. Faraday Soc.*, 1931, **27**, 629.

[42] *J. Ind. Eng. Chem.*, 1922, **14**, 1120.

[43] "Fluidity and Plasticity" (McGraw-Hill Book Co.), 1922; and earlier papers.

[44] *Sprechsaal*, 1905, **38**, 597, 881, 1625; 1906, **39**, 1167, 1184.

[45] *J. Amer. Ceram. Soc.*, 1928, **11**, 542.

than when deflocculated. Use is made by ceramists of this fact in adding sodium silicate and similar deflocculants to the casting slip. When deflocculated, the clay will pour at a low water content, and hence a minimum amount of water has to be extracted by the casting to produce a hard body. G. W. Scott Blair and E. M. Crowther,[46] and later, Schofield and Scott Blair,[47] have studied the characteristics of the flow of clay pastes in considerable detail, and have demonstrated the great complexity of the system. An account of these studies is outside the scope of this Report.

The phenomenon of deflocculation is met with in " alkali " soils.[48] Where, as is frequently the case, the condition has been brought about by the accumulation of sodium salts in the soil, no deterioration in the physical condition occurs while the salt content remains above a certain critical amount. The reduction of the salt concentration below this value, however, brings about a complete change which, by analogy with the behaviour of the dilute suspensions discussed earlier in this report, is recognised as deflocculation. The soil, although wet and sticky, allows water to percolate only very slowly. The presence of soluble calcium salts in sufficient quantity prevents this deflocculation. In reclamation work, calcium sulphate, and sometimes calcium chloride, are spread over the surface before irrigating, or, if the soil contains calcium carbonate, a salt resistant crop is grown and ploughed under, using only a small amount of water. The carbon dioxide thereby evolved brings sufficient calcium bicarbonate in solution.

[46] *J. Physical Chem.*, 1929, **33**, 321.

[47] *Ibid.*, 1930, **34**, 248; 1931, **35**, 1212; G. W. Scott Blair, *ibid.*, p. 374; *Soil Sci.*, 1931, **31**, 291.

[48] (Sir) E. J. Russell, " Soil Conditions and Plant Growth," Sixth Edition, 1932, Chap. 4 (Longmans).

THE STRUCTURE OF SIMPLE MOLECULES

I. METHODS.

THE last few years have seen the development of a variety of quite distinct methods of physical investigation, throwing light on the details of molecular structure; so that it is now possible to elucidate the structure of covalent molecules by the converging results of a series of independent physical arguments. These methods are applicable in principle to complex as well as simple molecules, but their results are naturally more easily interpreted in the simpler cases. The application of wave-mechanics to the sharing of electrons has been greatly extended in the last two years; [1] of special interest for the subjects here discussed are the work of E. Hückel,[2] giving a theoretical basis for the absence of free rotation of doubly linked atoms, and two recent papers by L. Pauling; [3] in the first of these he calculates the valency angles, and finds that while in a 4-covalent atom they should normally have the tetrahedral value of 109·5°, with atoms of covalencies of 2 or 3 the angles are approximately 90°. Another important conclusion is that bivalent nickel, palladium, and platinum and other transitional elements should form 4-covalent compounds in which attached groups occupy the corners of a square with the metallic atom at its centre.[4] W. Heisenberg has, however, pointed out [5] that the basis of these calculations, which is also that of the work of Heitler and London, is not quite certain. Pauling's second paper deals with the conditions under which links of one and of three electrons are possible.

The number of properties of a molecule which can be investigated, and which are of greater or less value for the determination of structure, is very large. In this Report only a few of the more important will be discussed; these are the distances between the linked atoms, the force constants of the links (the forces required to move the atoms further apart or nearer together), the mean restoring forces during vibration, the energy involved when the atoms form the link, the angles between the valencies, and the dipole moments of the links, which express the ratio in which the linking electrons are shared between the atoms.

[1] See *Ann. Reports*, 1930, **27**, 10. [2] *Z. Elektrochem.*, 1930, **36**, 641.

[3] *J. Amer. Chem. Soc.*, 1931, **53**, 1367, 3225. See also J. C. Slater, *Physical Rev.*, 1931, **37**, 481.

[4] See p. 399.

[5] " Chemistry at the Centenary (1931) Meeting of the British Association."

The experimental methods concerned involve the use of radiations from the far infra-red down to X-rays, and, recently, electron waves; the measurement of the heat properties; and the determination of dielectric constants. Since the same information is often given by very different methods, it is convenient to discuss the methods first and the results later.

Spectroscopic Methods.

Molecules can absorb or emit energy in three ways: (1) by the change of an electron from one orbit to another, (2) by a change of the oscillational or vibrational energy of the atoms, and (3) by a change in the rotational energy. The energies concerned can be expressed in calories per gram-molecule, in "volts," or more correctly electron volts (the unit being the energy gained by an electron in falling through a potential drop of one volt), or in terms of the wave-length, wave-number, or frequency of the radiation emitted or absorbed. The following table gives an idea of the magnitude of the three kinds of quanta concerned.

	Energy.				
Transition.	Volts.	Kilocals./ g.-mol.	Wave-length, Å.	Wave-number, cm.$^{-1}$.	Separation in band of 6000 Å., Å.
Electronic	1—10	23—230	12,350—1,235	8,100—81,000	(6000)
Oscillational or vibrational	$\frac{1}{10}$	2·3	123,500	810	300
Rotational	$\frac{1}{1000}$	0·023	1235×10^4 or 1235 μ or 0·1235 cm.	8·1	3

The methods may be classified according to the region of the spectrum examined.

Far Infra-red Absorption Spectra of Gases.[6]—Molecules possessing an electric moment can absorb far infra-red radiation by an increase of rotational energy ($m \longrightarrow m + 1$). Hence a diatomic molecule (with one degree of freedom) gives an absorption spectrum in this region of almost equally spaced lines, the frequencies of which were shown by Heisenberg to be:

$$\nu = mh/4\pi^2 J$$

where m is an integer, and J is the moment of inertia of the molecule. Since we know the masses of the atoms, this enables us to measure r, the distance between the nuclei, from the relation:

$$J = \frac{M_1 M_2}{M_1 + M_2} \times 1{\cdot}65 \times 10^{-24}\, r^2 \text{ g.-cm.}^2$$

where M_1 and M_2 are the gram-atomic weights of the atoms. This

[6] See "Das Ultrarote Spektrum," C. Schaefer und F. Matossi (Springer, Berlin, 1930).

method has been applied, for example, to determine the interatomic distances in the hydrogen halides.[7]

In principle, this method can be applied to more complex molecules which give several different moments of inertia. The experimental technique of this region (23—200 μ) is, however, particularly difficult, from the feebleness of the radiation obtainable, the lack of transparent materials for the construction of cells and prisms, and the overlapping of different spectral orders consequent on the necessity of using gratings for a range of frequencies of many octaves. Hence most investigators of infra-red spectra have contented themselves with the somewhat easier technique of the near infra-red region.

Near Infra-red Absorption Spectra.—When the electric moment of a molecule is changed by the absorption of a quantum of vibrational energy, that molecule is capable of absorbing near infra-red radiation, and passing from one vibrational state (almost always $n = 0$) to another ($n = 1, 2, 3$, etc.). Such a transition is coupled with changes in the rotational state of the molecule, leading to an absorption band composed of lines given by the relation :

$$\nu = \frac{\Delta E_n}{h} + \frac{h[m_1(m_1 + 1) - m_2(m_2 + 1)]}{8\pi^2 J}$$

The usual rotational changes are $m \longrightarrow m + 1$ (P branch) and $m \longrightarrow m - 1$ (R branch); in special cases the Q branch ($\Delta m = 0$) is observed. These rotation-vibration spectra are investigated by the use of a source such as a Nernst glower, an absorption cell with suitable transparent ends, mirrors to focus the radiation, a prism of rock-salt or sylvine, generally combined with a grating, to disperse it, and a thermopile to record the transmission.

Diatomic molecules such as the hydrogen halides show a simple series of absorption bands corresponding to the vibrational transitions $0 \longrightarrow 1, 2$, etc., each with a rotational fine structure from which values of J, and so of r, can be obtained for the molecule in its non-vibrating state and for the molecule with one or more vibrational quanta. As would be expected, the values of r increase with the vibrational energy of the molecule.

The spectra obtained from polyatomic molecules are naturally very complex, owing to the interpenetration of bands corresponding to different transitions, and the greatest interest centres at present round triatomic molecules such as H_2O. The results so far obtained must be regarded as provisional until the identification of the frequencies observed with particular transitions is more definitely

[7] M. Czerny, *Z. Physik*, 1923, **16**, 321; 1925, **34**, 227; 1927, **44**, 235; **45**, 476.

established. When correct identifications are made, the structure of a simple molecule can be deduced from considerations of two kinds.

(*a*) From the number of moments of inertia of the molecule, given by the fine structure of the infra-red bands. A linear triatomic molecule is easily differentiated in this way from a triangular one, and from the values of the moments the dimensions of the molecule can be obtained.

(*b*) From the number and values of the vibrational frequencies of the molecule. For a triangular triatomic molecule the angle at the apex between two similar bonds can be found from the three characteristic frequencies.[8, 9]

Raman Spectra.[9, 10]—When monochromatic light is scattered by the molecules of a transparent substance, the greater part has its frequency unchanged, but a small fraction is scattered at discrete other frequencies, the frequency differences between exciting and scattered lines corresponding to changes in one of the characteristic vibrational or rotational levels of the molecule. Rotational transitions are indicated by lines very near the spectral line scattered without frequency change; vibrational transitions by lines much further away. The latter are not coupled with simultaneous rotational changes, *i.e.*, they correspond to Q branches ($\Delta m = 0$), and therefore afford much clearer data on vibrational levels than do the near infra-red absorption bands, which are restricted to vibration changes involving a change of electric moment, and are complicated by P and R rotational branches. Raman lines are excited for all types of vibration in which there is a change of polarisibility with phase.[11] The two methods of investigation are thus supplementary to one another, and, besides directly affording material on which to base views of molecular structure, are, taken together, of very great importance in interpreting the complexities of electronic band spectra (p. 371).

The study of this new scattering phenomenon, predicted by A. Smekal [12] and first discovered by (Sir) C. V. Raman,[13] has now been taken up by a great number of investigators. The scattered lines

[8] N. Bjerrum, *Ber. deut. physikal. Ges.*, 1914, **16**, 737; R. C. Yates, *Physical Rev.*, 1930, **36**, 555.

[9] K. W. F. Kohlrausch, "Der Smekal-Raman Effekt," Springer, Berlin, 1931.

[10] C. Schaefer and F. Matossi, "Der Ramaneffekt," Borntraeger, Berlin, 1930.

[11] A. S. Ganesan and S. Venkateswaran, *Ind. J. Phys.*, 1929, **4**, 195.

[12] *Naturwiss.*, 1923, **11**, 873.

[13] C. V. Raman and K. S. Krishnan, *Nature*, 1928, **121**, 501, 619; *Ind. J. Physics*, 1928, **2**, 399.

are faint, and most experimenters have used modifications of a technique due to R. W. Wood.[14]

A. Dadieu and K. W. F. Kohlrausch [15] were the first clearly to show that particular atomic groupings give characteristic Raman lines. They identified the single Raman line observed for diatomic molecules with the natural frequency of the system as given by the ordinary mechanical expression :

$$\text{frequency} = \frac{1}{2\pi}\sqrt{\frac{f}{M}}$$

or

$$f = 5{\cdot}86 \times 10^{-2} M\omega^2 \text{ dynes/cm.}$$

where ω = frequency (sec.$^{-1}$), M = the reduced mass of the system ($1/M = 1/M_1 + 1/M_2$), and f = the force constant of the link which is vibrating, that is, the force which arises when the nuclei are displaced unit distance from their equilibrium position. The force constant f is approximately proportional to the energy of dissociation of the link to which it refers, as is shown by the constancy of the empirical expression :

$$\nu(\text{cm.}^{-1})\ \sqrt{M(\text{gms.})/A}$$

(where A is the dissociation energy of the link in kilocalories per mole), which varies over a wide range of examples from 290 to 390.

The amplitude of vibration a can be obtained from the relation :

$$a\ (\text{cm.}) = 8{\cdot}187 \times 10^{-8}\ \sqrt{1/M\omega}$$

from which can be found the mean restoring force during the vibration :

$$K\ (\text{dynes}) = fa/2 = 24{\cdot}0 \times 10^{-10}\ \sqrt{\omega^3 M}$$

Values of the quantities f and K are given in Table I (p. 401).

In the case of more complex molecules, lines of particular frequencies varying only slightly in different compounds have been identified with particular linkages, and in some cases with particular types of vibration of those linkages, *i.e.*, the bending or stretching of the link.[16] As with the near infra-red measurements, the number and value of the vibrational frequencies, and of the rotational frequencies of the Raman lines, enable us to deduce the size, shape, and force constants of molecules that are not too complex. An interesting development has been the construction of molecular models with masses and springs which closely imitate the Raman spectra of carbon tetrachloride, benzene, etc.[17]

[14] *Physical Rev.*, 1930, **36**, 1421; *Trans. Faraday Soc.*, 1929, **25**, 792; N. N. Pal and P. N. Sen Gupta, *Ind. J. Phys.*, 1930, **5**, 609.

[15] *Ber.*, 1930, **63**, [*B*], 251.

[16] D. H. Andrews, *Physical Rev.*, 1930, **36**, 544.

[17] C. F. Kettering, L. W. Shutts, and D. H. Andrews, *ibid.*, p. 531.

Raman data, when fully interpreted, promise to provide more accurate knowledge of the structure of molecules than any other spectral method. Much work is now being done in following the shift of particular lines associated with the vibration of particular linkages (and so related to their force constants) in series of similar compounds, and from work of this kind a great deal of light is likely to be thrown on constitutive problems of quite complex organic compounds.[15, 18, 155]

Electronic Band Absorption Spectra.—When molecules absorb radiation at frequencies which produce an electronic transition, simultaneous changes also occur in the vibrational and rotational states of the molecule, leading to the production of a complex band system associated with each electronic transition.[19] The case of diatomic molecules has been very fully investigated, and great advances have been made in such problems as the coupling of large or small vibration changes with the electronic transition, and the effect of nuclear spin on the rotational states of the molecule. Such completeness of detail is unlikely to be attained for more complex molecules for some time; nevertheless it is possible in certain cases to arrive at a structure for a polyatomic molecule from a consideration of its electronic absorption spectrum in the gaseous state. The analysis of the spectrum is facilitated by introducing the frequencies of the normal molecule as obtained from Raman or near infra-red data. In favourable cases the moments of inertia of the molecule both in the normal and in the excited state can be calculated from the fine structure of the vibration bands, while from the relationships of the frequencies of the vibration bands themselves the force constants of the two states can be obtained. The method is thus very similar to that used with Raman or near infra-red spectra, with the addition that structures can be deduced both for the normal and for the electronically excited molecule. It has, however, serious limitations; the complexity of the spectrum is liable to lead to incorrect assignment of lines; the spectrum may be structureless, as with HI or Cl_2O; and where large moments of inertia are involved it is difficult to obtain satisfactory resolving power for the examination of the rotation lines.

In Table I are given data on the structure of molecules obtained by spectral methods. Entirely satisfactory results by any of these methods are at present limited to diatomic and rectilinear triatomic molecules. Of more complex molecules, H_2O [140, 148, 149], H_2S [149, 143], ClO_2 [154], and SO_2 [152] are undoubtedly triangular, NH_3 [141] is pyramidal,

[18] Dadieu and Kohlrausch, *loc. cit.*, (ref. 15); M. E. High, *Physical Rev.*, 1931, **38**, 1837; W. D. Harkins and H. E. Bowers, *ibid.*, p. 1845.

[19] *Ann. Reports*, 1926, **23**, 296.

and $COCl_2$ [151], S_2Cl_2, $SOCl_2$ [152], and CH_2O [144] are **Y**-shaped, but the values of the angles and distances at present obtained by spectral methods must be regarded as subject to revision.

X-Ray Methods.

These may be discussed under two heads, according as the material examined is a solid or a gas.

Determination of Crystal Structure by X-Rays.—This application of *X*-rays is too familiar to need detailed discussion here.[20] It depends on the power of the atoms, or rather of their electrons, to scatter the *X*-rays, so that the crystal can be used as a grating, the interatomic distances being of the same order as the wave-length of the radiation. Hence, if the wave-length is known (this can now be checked by the use of ruled gratings at a very small glancing angle), the spacing of the atomic grating can be determined. If the arrangement of the atoms in the crystal can be ascertained (alternative arrangements are sometimes possible), we can calculate from the measurements the distances between pairs of atoms. For the simpler structures these distances can be determined with an accuracy of 0·05—0·1%.[21] The method was extended by P. Debye and P. Scherrer [22] to crystal powders, so that it can be used where it is not possible to obtain single crystals of any size.

X-Ray Interference in Vapours.—This is a new development of great importance, which we owe to Debye and his pupils.[23, 24, 25, 26, 27] In the solid state the molecules are under some restraint, and the distances between the atoms, and more especially the valency angles, may be thereby modified. Debye and Scherrer's application of their powder method to liquids leads to great difficulties of interpretation, as we are not sure whether the distances we are measuring are between atoms of the same or of neighbouring molecules.[28] With a gas these difficulties do not arise; the regular distances must be between atoms of the same molecule in an unconstrained state. On the other hand the scattering power of the quantity of material

[20] See W. H. and W. L. Bragg, "*X*-Rays and Crystal Structure," 1925; R. W. G. Wyckoff, "The Structure of Crystals," 1924. 2nd Edn., 1931.

[21] V. M. Goldschmidt, *Geochem. Vert.*, 1927, **8**, 21.

[22] *Nach. Ges. Wiss. Göttingen*, 1916, 16; *Physikal. Z.*, 1916, **17**, 277. See also A. W. Hull, *Physical Rev.*, 1917, **10**, 661.

[23] P. Debye, L. Bewilogua, and F. Ehrhardt, *Physikal. Z.*, 1929, **30**, 84; P. Debye, *ibid.*, p. 524; H. Mark, *Z. angew. Chem.*, 1931, **44**, 125.

[24] P. Debye, *Physikal. Z.*, 1930, **31**, 142, 419.

[25] P. Debye, *Z. Elektrochem.*, 1930, **36**, 612.

[26] L. Bewilogua, *Physikal. Z.*, 1931, **32**, 265.

[27] H. Gazewski, *ibid.*, p. 219.

[28] See, however, Debye, *ibid.*, 1930, **31**, 348; Debye and H. Menke, *ibid.*, p. 797.

contained in a small volume of the gas is minute in comparison with that in a solid or liquid, and prolonged exposures are necessary. Originally some 24 hours were required, but this has now been reduced to 4 or 5. The method is essentially the same as that used for powders or liquids, a narrow beam of X-rays being passed through a small chamber through which the vapour of the substance is flowing, and the scattered rays being received on a photographic plate. The calculation of the interatomic distances from the trace on the plate involves considerable mathematical difficulties; allowance must be made for the distortion of the electronic orbits, and also for the Compton effect. These difficulties have now, however, been overcome,[29] and it has been possible to measure the distances with an accuracy greater than 1%.

Method of Electron-Ray Interference.

We now know that electrons in motion are accompanied by, or consist of, systems of waves whose length is given by the de Broglie relation :

$$\lambda = h/mv$$

where m is the mass and v the velocity of the electron.[30]

When a narrow pencil of electrons passes through a vapour, the electrons are scattered, and their waves produce interference patterns which can be received on a photographic plate. Thus the general nature of the method is the same as in Debye's experiments with X-rays. The necessary corrections for determining the distances have now been worked out,[31] and the results agree well with those obtained by the X-ray method : thus for the distances between the chlorine atoms in carbon tetrachloride R. Wierl [31, 32, 33, 34, 35] found 2·98 Å. and Debye 2·99 ± 0·03 Å. The relative accuracy of the two methods has been in dispute, but we may conclude [36] that the errors of the electron ray method are slightly the larger. It has, however, certain great practical advantages over the X-ray method. The interaction between the electrons and the

[29] For a general account, see Debye, in " Chemistry at the Centenary (1931) Meeting of the British Association."

[30] For its experimental verification, see G. P. Thomson, *Nature*, 1928, **122**, 279; " Wave Mechanics of Free Electrons," New York, McGraw Hill Book Co., 1930.

[31] H. Mark and R. Wierl, *Z. Physik*, 1930, **60**, 741. See also Mark and Wierl, " Die experimentellen und theoretischen Grundlagen der Elektronenbeugung," Berlin, Borntraeger, 1931; " Elektroneninterferenzen," Leipziger Vorträge, 1930, p. 13; *Ann. Reports*, 1930, **27**, 31.

[32] *Z. Elektrochem.*, 1930, **36**, 675. [33] *Naturwiss.*, 1930, **18**, 205.

[34] Wierl, *Physikal. Z.*, 1930, **31**, 366, 1028.

[35] *Ann. Physik*, 1931, **8**, [v], 521.

[36] L. Bewilogua, *Physikal. Z.*, 1931, **32**, 114.

molecules of a gas is much more intense than that of X-rays, and the electrons have a much stronger photographic effect; these two causes cut down the time of exposure to not more than 1/10,000 of that required for X-rays. In Wierl's experiments electrons of about 40 kilowatts energy (wave-length 0·06 Å.) were used, and the time of exposure was not more than a few tenths of a second. This is more than a mere practical convenience. Many organic compounds decompose far below the temperatures at which they boil under atmospheric pressure, and it is thus impossible to obtain their vapours except at great tenuity; such substances could scarcely be examined by the X-ray method, as the feeble scattering would necessitate enormously long exposures, whereas with electron rays quite short exposures would suffice.

The electron ray method is equally applicable to solids, and here it has another advantage over the use of X-rays. Owing to the more intense interaction of the electrons with the molecules, they penetrate a very much shorter distance into the material than X-rays, and so give us more information about the state of the surface layers.

Heats of Formation of Links.

The energy evolved when two atoms form a covalent link by sharing a pair of electrons (or absorbed when this link is broken) is a magnitude of obvious importance for characterising the link, and determining the thermodynamic stability of the molecule produced. For diatomic molecules this can be measured directly by various methods; for others it can be calculated if we know the heat of formation of the molecule from its elements in their ordinary states (*e.g.*, solid carbon, gaseous hydrogen, oxygen, nitrogen, etc.), and also the heat required to convert these elements from their ordinary states into atoms—the heats of atomisation.

Heats of Atomisation of Diatomic Molecules.[37, 38, 39, 40, 41, 42]—(a) When a diatomic molecule composed of two similar atoms can be dissociated thermally to a measurable extent, the heat of atomisation or linking can be determined from the change of the dissociation constant with temperature, by means of the van 't Hoff isochore. In this way the molecules Cl_2, Br_2, I_2 and H_2 can be examined.

37 R. T. Birge, Molecular Spectra in Gases, Bull. Nat. Res. Council, 1926, **11**.

38 H. Sponer, "Optische Bestimmung der Dissociationwärme von Gasen," *Erg. exakt. Naturwiss.*, 1927, **6**.

39 R. Mecke, "Bandspektra," Handb. Phys., 1929, **21**.

40 G. Herzberg, "Die Prädissoziation und verwandte Erscheinungen," *Erg. exakt. Naturwiss.*, 1931, **10**.

41 M. Rabinovitsch, *Z. Elektrochem.*, 1931, **37**, 91.

42 For complete literature, see Landolt–Börnstein, 5te Auflage, Zweiter Ergänzungsband, 1931, p. 1614, etc.

(b) The absorption bands of certain molecules (halogens, ICl, O_2) corresponding to an electronic excitation show a vibration band structure which converges to a sharp limit (accurately obtainable by a very short extrapolation of the band series), beyond which is a continuous band stretching towards the short wave part of the spectrum. Franck has shown that the energy corresponding to this limit is to be identified with the heat of dissociation of the molecule—not, however, into normal atoms, but into one normal and one excited atom. If the excitation state of the second atom can be identified, and its energy subtracted from that corresponding to the spectroscopic dissociation, the normal dissociation energy is obtained. This method is capable of an accuracy of 0·2 kilocalorie if no error is made in arriving at the state of the excited atom produced. The excitation state is found from an exact knowledge of the spectroscopic terms for the atom, together with the values of the normal (thermal) dissociation heat derived from methods less refined in character but not subject to this uncertainty as to the states of the products of dissociation.

(c) The type of spectrum in (b) is shown only by molecules in which the internuclear distance is greatly altered by electronic excitation. In other cases, direct observation of the convergence limits is not possible, because states of high vibrational quantum number are improbable. Molecules possessing electric moments show in the infra-red region bands corresponding to increases in the vibrational energy of the non-electronically excited molecule, the convergence limit of which gives the dissociation energy of the link to which the vibration belongs. This method involves a long and uncertain extrapolation, and is not available for non-polar molecules such as N_2 or H_2, which cannot change their vibrational states in the non-electronically excited state by absorption. A more general method consists in an extensive and detailed analysis of the band systems shown by a molecule both in absorption and in emission. It is then possible in some cases to arrive at the values of the different electronic energy levels of the molecule, and at those of the lower vibrational sub-levels associated with them. A long extrapolation of these vibrational sub-levels, varying in accuracy in different cases, and a determination of the distances of the limits from the ground level provide values for the heat of dissociation of the molecule, either into normal atoms if the sub-levels belong to the ground state, or into one normal and one excited atom if they belong to an excited state. In the latter event means must be found for specifying the excited state of the atom produced. By this method a very large number of dissociation energies have been estimated, such as those of the molecules H_2, Se_2, Te_2, CO, NO, AgCl, HgCl, LiH, as well as of

molecules not easily accessible to the chemist, as N_2^+, O_2^+, C_2, CN, SiN, BO, TiO, CO^+, SO, CS, HgH, Li_2, Na_2, K_2.

(d) The heat of dissociation D_{N_2} of the molecule N_2 has been obtained from that of the molecule N_2^+, $D_{N_2^+}$ (method c), by making use of the relation :

$$D_{N_2} = D_{N_2^+} + I_2 - I_1$$

where I_1 and I_2 are respectively the energies of ionisation of the neutral atom and the neutral molecule, which are obtainable from spectroscopic data and critical potential measurements. An accurate solution of a problem of this kind requires precise identification of measured data with particular energy states, which at last seems to have been achieved in this case.

Application to Polyatomic Molecules.—The sum of the energies of the links in a polyatomic molecule is directly obtainable by a combination of the ordinary thermochemical heat of formation of the substance with the heats of atomisation of the elements composing it. Where the ordinary heats of formation of the gaseous molecules refer to the elements in a solid or liquid state, correction must be made for the latent heat of fusion and of volatilisation of that element. Many heats of linkage of this kind, as, for example, that of PH_3, cannot yet be estimated for lack of the appropriate data ; in this case, for phosphorus. Of the greatest importance is the question of the heats of linking in carbon compounds. The link energies in molecules of the type CH_4, CCl_4, CO_2 can be found if the latent heat of volatilisation of solid carbon to carbon atoms is known. The most probable value of this quantity at the ordinary temperature is 150 kilocalories, as the values of the C–H link deduced from it are fairly close to those obtained from the extrapolated convergence of infra-red bands of organic substances (see above) and from predissociation spectra, as described below.

When the molecule contains more than one kind of link we can make progress only if we assume that the energies of particular links remain sensibly constant in different compounds. This assumption cannot be true, but it appears to be nearly so for related compounds. For example, by assuming that the link energy of C–H remains constant, the values obtained for the link C·C from the heats of formation of the saturated paraffins up to C_{10} do not vary beyond the experimental error. For this calculation any heats of formation which refer to the liquid paraffins must be corrected for the latent heats of volatilisation, which can conveniently be obtained from H. von Wartenberg's formula [43] with a further correction to reduce the value to the ordinary temperature. Similarly, from data for aromatic hydrocarbons, consistent values for the energies of

[43] *Z. Elektrochem.*, 1914, **20**, 444.

the C–H and C–C links, but different from those for the paraffins, are obtainable. By extending the assumption into regions where it cannot be so accurate, and making use of the heats of formation of ethers, aldehydes, esters, amines, unsaturated hydrocarbons, etc., fairly consistent values can be obtained for the energies of such links as C—O, C=O, N—H, C=C, C≡C, C—N, etc.

Predissociation Spectra.—Certain molecules show, at points in their vibration-rotation absorption spectra associated with an electronic excitation, a fusion of the rotation lines within the vibration bands, which can most simply be interpreted as the formation of unstable molecules which dissociate into two atoms or residues.[44] The energies corresponding to these limits are close to (though greater than) those of the links which are broken. In this way the link energy in the S_2 molecule can be obtained, as well as approximate values for the link energy of C–H and C–C in aldehydes and ketones.

Other Methods.—There are a few other methods of estimating link energies which are less accurate or less important.

(a) *Photosensitisation.* An atom is excited to a known state by absorption, and allowed to pass on this energy by collision to a molecule which is dissociated if the energy available is greater than and close to its dissociation energy. The heat of dissociation $H_2O \longrightarrow H + OH$ can be roughly estimated in this way,[45] which is of limited application.

(b) *Chemiluminescence.* The energy of combination of two atoms, *e.g.*, of Na and Cl, to give a molecule can be passed by collision to another atom, which is thereby raised to excited states recognisable by their fluorescent emission spectra. The highest emission state observable gives a lower limit for the heat of linkage of the molecule formed.

(c) *Photometric methods.* Where the molecule formed is in equilibrium with its dissociation products, as in $2BrCl \rightleftharpoons Br_2 + Cl_2$,[46] its energy of linkage can be calculated by applying the van 't Hoff isochore to its equilibrium constant, found by estimating optically the concentrations of the reactants. This can be done by photometric means either on their absorption bands or on their fluorescent emission spectra, according to the case examined.

(d) *Molecular beam method.*[47] There are two methods based on the use of a " unidimensional " molecular beam of the substance.

(1) When the atom possesses a magnetic moment and the mole-

[44] K. F. Bonhoeffer and A. Farkas, *Z. physikal. Chem.*, 1928, **134**, 337.

[45] E. Gaviola and R. W. Wood, *Phil. Mag.*, 1928, **6**, 1191; H. Senftleben and (Frl.) I. Rehren, *Z. Physik*, 1926, **37**, 529.

[46] W. Jost, *Z. physikal. Chem.*, 1931, [*A*], **153**, 143.

[47] See further, p. 381.

cule does not (Li_2, Na_2, K_2, Bi_2), the former only is deflected in an inhomogeneous magnetic field, so that the atoms and molecules can be collected separately on a plate and their relative amounts estimated. From the temperature variation of the proportions the heat of dissociation can be calculated.[48]

(2) The relative proportion of atoms and molecules in a molecular beam can be found by the spreading of a rapidly rotating beam. The heat of dissociation can then be found as before from the temperature coefficient of the mass-action constant.[49]

Measurement of Dipole Moment.[50]

If the centres of action of the positive and negative parts of a molecule do not coincide, the molecule is polar: it is electrically equivalent to a rod with a positive charge at one end and a negative charge at the other, and in an electric field it tends to arrange itself with its negative end towards the positive pole. Its dipole moment is given by the product of one of the charges into the distance between them. Every isolated atom is non-polar. When two atoms share electrons, if they share them equally, the molecule produced will also be non-polar, but if unequally, it will be polar,[51] the atom which has the greater share being at the negative end of the dipole. Experiment shows that covalent links between unlike atoms are in general polar.

The methods of measuring dipole moments depend almost wholly on the determination of dielectric constants. If ε is the dielectric constant of a medium of density d, containing the molar fractions f_2, f_1 of two substances of molecular weight M_2, M_1, the "mean molecular polarisation" P_{12} is related to the separate molecular polarisations P_2, P_1 by:

$$P_{12} = P_1 f_1 + P_2 f_2 = \frac{\varepsilon - 1}{\varepsilon + 2} \times \frac{f_1 M_1 + f_2 M_2}{d}$$

This relation depends on the Clausius–Mosotti equation, which takes no account of the mutual influence of the dipoles at close ranges; it can thus only be applied when the polar molecules are so

[48] A. Leu, *Z. Physik*, 1928, **49**, 498; Lewis, *ibid.*, 1931, **69**, 786.

[49] I. F. Zartman, *Physical Rev.*, 1931, **37**, 383.

[50] P. Debye, "Polar Molecules," 1929; C. P. Smyth, "Dielectric Constant and Molecular Structure," 1931. See also H. Sack, "Dipolmomente und molekulare Strukture," *Erg. exakt. Wiss.*, 1929, **8**, 307, and Leipziger Vorträge, 1929.

[51] The words polar and non-polar are used throughout in their strict physical sense, and mean possessing or not possessing a dipole moment. To this meaning they should always be confined: their use in other senses, for example, to distinguish ionised from non-ionised links, or associated from non-associated liquids, has led to much confusion.

far apart that this influence can be neglected, *i.e.*, to a gas, or a dilute solution of a polar substance in a non-polar solvent.

A molecule can be polarised by the electric field in three ways :

(1) The electrons are displaced with respect to the nuclei. This gives the electron polarisation P_E. This change is very rapid, of the order of 10^{-15} sec. : it thus follows the oscillations of the electric field up to the far ultra-violet.

(2) The nuclei themselves may be displaced owing to the shift of the electrons. This atomic polarisation, P_A, is less rapid, about $10^{-12} - 10^{-13}$ sec. : it follows the field up to frequencies in the infra-red.

(3) If the molecule has a permanent dipole moment, it will tend to orient itself in the field. This orientation polarisation, P_O, is relatively slow, requiring about 10^{-10} sec.

The dielectric constants themselves are commonly measured with wireless waves of the order of 100 m. wave-length, that is, with a period of about 3×10^{-7}, so that the results include all three forms of polarisation. The relation of the molecular polarisation to the dipole moment was shown by Debye to be given by :

$$P = \frac{4\pi}{3} . N\left(\alpha_0 + \frac{\mu^2}{3kT}\right)$$

where N is the Avogadro number, α_0 the electronic and atomic polarisations, μ the dipole moment, k the gas constant per molecule, and T the absolute temperature. Hence in order to measure μ we require to eliminate P_E and P_A. This can be done in two ways.

(A) Temperature method. P_E and P_A are independent of temperature, whereas P_O, as the equation shows, is inversely proportional to it, since the thermal agitation opposes the orientation of the dipoles. Hence if P is determined at several temperatures, and the values are plotted against the reciprocal of the temperature, the result will be a straight line, which will be horizontal if the substance is non-polar, and if it is polar will be inclined to the horizontal at an angle from which μ can be calculated.

This is the most accurate method, since it eliminates both the electronic and the atomic polarisation.

(B) Optical method. A simpler but rather less accurate method devised by Debye and Lange is that in which the electron polarisation is determined by using oscillations which are too rapid to cause orientation, *i.e.*, the waves of visible light, of which there are about 10^{14} per second. The molecular refractivity, calculated by the Lorenz–Lorentz formula, is the electronic polarisation. Hence if we subtract the molecular refractivity from the total polarisation as measured by wireless waves, we get the value of $P_A + P_O$. P_A

cannot be determined by this method. Its amount is usually small: for a substance of fairly large moment the orders of magnitude are P_E 20, P_A about 5, P_O 200. Debye has pointed out that some correction is automatically made for P_A if we calculate the refractivity not, as should strictly be done, for infinite wave-length, but from the refractive index for sodium light. This uncertainty about P_A is the weakness of the otherwise most convenient optical method. Where the moment is large the error introduced is not serious, but where it is small or zero, this term may become of greater importance; any value of μ less than about $0{\cdot}4 \times 10^{-18}$ obtained by this method may mean that the substance is non-polar.

Another method sometimes employed to obtain P_E and P_A is to measure the dielectric constant of the solid substance. We cannot, however, always be sure that orientation is impossible in the solid.

Most of the values of the dipole moment have been obtained by the optical method, and in solution. Many substances have been shown to give the same values of the moment in the gaseous state, and in solution in a variety of non-polar solvents such as benzene, carbon disulphide, carbon tetrachloride, and the liquid paraffins. Benzene is the most commonly used; but recent work has shown that this particular solvent can sometimes combine with a solute in such a way as to affect its moment; thus iodine has a moment of 1·0 [52] in benzene, but zero in hexane and *cyclo*hexane : [53] aluminium bromide a moment of 4·89 in benzene and zero in carbon disulphide.[54]

Molecular Beam Method.—This is an entirely different method, which, although its results are so far less accurate than those of the dielectric methods, can sometimes be used where they fail, and in any event is of value as giving an independent confirmation of the truth of the general theory. It is founded on the famous atomic beam experiments by which Stern and Gerlach determined the magnetic moments of atoms. Its first electrical application was due to E. Wrede,[56] who showed in this way that the molecules of the alkaline halides, which cannot be investigated by the dielectric methods, have moments of the order of 10×10^{-18}. It has since been greatly extended by J. Estermann.[57] The substance to be investigated is heated in a minute oven to a temperature at which it has a perceptible

[52] The moments of polar molecules have values up to about 8×10^{-18} E.S.U. To save space they are all multiplied by 10^{18}.

[53] H. Müller and H. Sack, *Physikal. Z.*, 1930, **31**, 815.

[54] E. Bergmann and L. Engel, *ibid.*, 1931, **32**, 507.

[55] For a full account of this method and its various applications, see R. G. S. Fraser, "Molecular Rays," Cambridge, 1931.

[56] *Z. Physik*, 1927, **44**, 261.

[57] *Z. physikal. Chem.*, 1928, *B*, **1**, 164; **2**, 287; Leipz. Vortr., 1929, 17.

but very small vapour pressure. A stream of molecules, too far removed from one another to collide, and with a velocity given by their temperature, in accordance with the gas laws, issues through a narrow (0·01 mm.) slit into a high vacuum, and by means of a second slit is cut down to a narrow and very thin ribbon of rays. This is passed through a highly inhomogeneous electric field, and then received on a brass plate cooled with liquid air, and the trace which the molecules form is observed with a microscope.

In the absence of the field the molecules go straight through the apparatus, and condense on the plate in a narrow vertical line, less than 0·15 mm. wide. When the field is put on (Estermann used 21,000 volts) it affects even non-polar molecules, since the electron polarisation causes an induced dipole, and so they move towards the stronger part of the field; but the trace shifts as a whole. If, however, the molecules are polar, the effect of the field on any one depends on the inclination of its dipole to the field, and so the trace is broadened to an extent depending on the moment of the molecule. So far it has not been found possible to deduce more than a rough estimate of the moments.

This method can be used with substances which are not volatile enough for the dielectric constant of their vapours to be measured, and which are not soluble enough in non-polar solvents for the solution method to be practicable. Its most remarkable success was with pentaerythritol, $C(CH_2{\cdot}OH)_4$, m. p. 250—255°, which was shown to have a moment of about $2{\cdot}0 \times 10^{-18}$.

II. Results.

Dimensions.

The methods already described for measuring the lengths of the links between atoms give us the distances between the atomic nuclei. To make them intelligible we have to try to determine the "radii" of the atoms concerned. In the light of modern theories of atomic structure it is difficult to say exactly what the "outside" of an atom means, or what its true radius is. For our present purpose this difficulty can be avoided by using the word radius in the sense of effective radius, as meaning the contribution which each atom makes to the length of the link with another atom.

As we have seen, the dimensions of links can be determined both in the solid and in the gaseous state. It does not seem that the state of aggregation makes much difference to the length of a covalent link; and this is to be expected, since the forces between the molecules of a covalent solid are small in comparison with those between the component atoms of the molecule: in carbon tetrachloride, for

example, the latent heats of fusion and evaporation are both about 7 kg.-cals. per g.-mol., while the separation of the CCl_4 molecules into their component atoms needs about 270 kg.-cals. On the other hand, in discussing the data derived from the study of solids, which are by far the most numerous, we have to deal with the distinction between the two kinds of link, electrovalent and covalent; this ambiguity does not arise with gases, since the only molecules which can be obtained in the gaseous state, except at very high temperatures, are covalent. But with solids both kinds of link occur, and it is clear, largely through the work of V. M. Goldschmidt,[58] that the nature of the link has an effect on its length. This conclusion, however, only emerges after a rather detailed examination of the facts. The values given by Goldschmidt and others for the radius of an atom in the neutral and ionised states differ widely (*e.g.*, K 2·27, K^+ 1·33; Cl 0·97, Cl^- 1·81 Å.U.); but the effects of a positive and a negative charge are in opposite directions; they therefore neutralise one another to a considerable extent in a salt, and while the radius of each atom is very different according as the link is ionised or covalent, the effect on the sum of the two radii, which is what is actually measured, is much less. In fact it is of the same order as that of two other influences which Goldschmidt has emphasized. The first is the deformation of the ions by one another, to which are due the small changes observed in the differences of the interatomic distances of, say, the sodium and potassium salts of the same halogen as we pass from one halogen to another: this may amount to as much as 5%. The second, which probably applies to covalent as well as to ionised links, is the effect of the type of lattice, of what Goldschmidt calls the "co-ordination number," which has nothing to do with the Werner theory, but is merely the number of nearest neighbours which the atom has in the crystal. As this number gets smaller the distances between the atoms decrease, and in extreme cases (going from 12 to 4) as much as 15%: the decrease is, however, sufficiently regular to be allowed for. When regard is had to these modifying influences, it can be shown that there is a definite change in the distance when the link passes from the electrovalent to the covalent form. In the compounds of silver and cadmium given in Table II (p. 402), those which are ionised in the crystal are distinguished by square brackets, and it will be seen that in all of these the observed distance is greater than that calculated for the covalent state. Often the distinction between the two kinds of link appears more clearly from the type of crystal

[58] "Geochemische Verteilungsgesetze," VII, Oslo, 1926; VIII, Oslo, 1927; *Ber.*, 1927, **60**, 1263. See also L. Pauling, *J. Amer. Chem. Soc.*, 1927, **49**, 765.

lattice, the covalent compounds favouring, as we should expect, the more open types, while true salts assume the most close packed form.

In considering molecular structure we are essentially concerned with the covalent link, and with the effective radii of neutral atoms.[59] A list of these radii for some of the more important elements is given in Table II. The constancy of these magnitudes, even under very diverse conditions of observation, is surprising. The distance between two singly linked carbon atoms is found from the crystal structure to be 1·54 Å.U. in diamond,[60] 1·6 in solid ethane,[61] 1·55 in the side chains of hexamethylbenzene,[62] and 1·58 in long-chain paraffins[63]; while by electron scattering we get 1·5 from the vapour of paraffins and naphthenes.[34] The "aromatic" link is 1·42 in graphite,[64] 1·45 in solid hexamethylbenzene,[62] 1·45 in solid naphthalene,[65] and 1·4 in benzene vapour as measured both by *X*-ray and by electron scattering.[34, 35] The double link C∶C is 1·35 in solid stilbene,[66] and 1·31 according to the spectrum of the Swan bands.[67] The agreement between the interatomic distances observed in compounds, and those calculated from the values for the elements, whether the data are got from the solid or the gas, and whether by means of the crystal structure, or the band spectra in any of their forms, or the scattering of *X*-rays or electrons, is remarkably close, not only among organic compounds, but generally, even among the compounds of the metals where these are not ionised; and it holds also with the hydrogen halides, in spite of the exceptional character of the hydrogen atom. A series of examples is given in Table II, the calculated values being obtained from the atomic radii in the same table. The values marked "corr." are corrected on the hypothesis that a double link is 14% and a triple 23% shorter than a single link. These are the observed differences with carbon (0·22 and 0·36 Å.U.); and while we do not know the effect on other elements, we may assume that it is of the same order, especially since the interatomic distances for carbon and the succeeding elements

[59] A remarkable series of simple relationships between the atomic radii (especially those of the metals) and the atomic numbers has been pointed out by W. Hume-Rothery (*Phil. Mag.*, 1930, **10**, 217).

[60] W. Ehrenberg, *Z. Krist.*, 1926, **63**, 320.

[61] H. Mark and E. Pohland, *ibid.*, 1925, **62**, 103.

[62] (Mrs.) K. Lonsdale, *Proc. Roy. Soc.*, 1929, **123**, 494.

[63] A. Müller, *ibid.*, 1927, **114**, 542; 1928, **120**, 437.

[64] E. Ott, *Ann. Physik*, 1928, **85**, 81.

[65] K. Banerjee and J. M. Robertson, *Nature*, 1930, **125**, 456.

[66] J. Hengstenberg and H. Mark, *Z. Krist.*, 1929, **70**, 283.

[67] Quoted by K. H. Meyer and H. Mark, "Aufbau d. hochpolymeren org. Naturstoffe," Leipzig, Akad. Verlagsges., 1930, p. 17.

present a much more regular series if they are corrected on this basis:

	C—C.	N≡N.	O=O.	F—F.
Observed	1·54	1·11	1·20	1·35
Correction	—	0·34	0·20	—
	C—C.	N—N.	O—O.	F—F.
Corrected	1·54	1·45	1·40	1·35

In polyatomic molecules the measurement of interatomic distances can also give us information about the angles between the valencies. The general question of stereochemical configuration will be discussed later,[68] but we may consider here the very remarkable investigations of Debye and of Wierl with their collaborators, by the *X*-ray and the electron method respectively, on the chlorinated methanes. They measured, with concordant results,[25, 26] the Cl,Cl distances in carbon tetrachloride, chloroform, and methylene chloride, and the C·Cl distance in methyl chloride. In the symmetrical CCl_4, the valency angles are all obviously 109·5°. From the observed Cl,Cl distance of 2·99 Å.U. this gives C·Cl as 1·82. In $H_3C{\cdot}Cl$, C·Cl has the same value. We can therefore assume that it has this length in the intermediate compounds as well, and this enables us to calculate the angles between the C·Cl valencies as follows:

Compound.	Cl,Cl.	Val. angle.
CCl_4	2·99	109·5°
$CHCl_3$	3·11	116·4
CH_2Cl_2	3·23	123·8

It is clear that with the successive replacements of chlorine by hydrogen the distance between the carbon and the chlorine remains constant, but the angle between the C·Cl valencies increases (as the Thorpe–Ingold theory assumes), and by about 6 or 7% on each replacement. The results are of great interest as giving us a definite idea of the extent to which the valency angles can be modified by the other groups present in the molecule.

The general conclusion to which the study of molecular dimensions leads is that in covalent links the effective radii are remarkably constant, and are but little affected either by the conditions of the molecule, whether solid, liquid, or gaseous, or by the other atoms which it contains. The angles between the valencies are much more subject to change. In the older stereochemistry great stress was laid on the valency angles, but relatively little attention was paid to the interatomic distances. It is now clear that the constancy of these two factors is in the reverse order.

Heats of Formation of Links.

As we have seen,[69] these values can be determined for diatomic molecules directly; for polyatomic molecules the sum of the values

[68] p. 398. [69] p. 375.

for all the links in the molecule can be calculated if we know the heat of formation of the molecule from its elements, and the heats of atomisation of those elements. If we are to obtain values for the individual links, we must assume that these are independent of the other links in the molecule, or that we know how the latter affect them.

The heats of atomisation of the elements, a knowledge of which is essential to the problem, have only become known with any accuracy in the last few years—even now only a limited number are known—and hence the subject is of comparatively recent development. One of the first to draw attention to it was K. Fajans,[70] who showed that the heat of rupture of the C–C link was almost the same in ethane and in diamond. Further investigations were made by A. von Weinberg,[71] A. Eucken,[72] H. G. Grimm,[73] and H. Wolff, and others; the results are summarised by Grimm [74] and by Eucken [75]; their data, however, need some revision in the light of later determinations of the heats of atomisation.

The last column of Table I contains a series of values of the heats of rupture of covalent links. For a diatomic molecule the heat of rupture of the link is twice the heat of atomisation. Two other values of the heat of atomisation should be added; for solid sulphur 65·6 and for solid carbon 150 kg.-cals. per gram-atom. The heat of rupture of the C–C link in solid carbon is of course half this, or 75 kg.-cals.

The values given in the table for compounds are mostly derived from their heats of combustion through the heats of formation. Where the links are all the same (H_2O, NH_3, CH_4), the value given is the total heat divided by the number of links. Where they are different, rather uncertain assumptions must be made as to the constancy of the heat of a particular link. With the organic compounds the value 93·6 for C–H (derived from methane) is used throughout. This is probably accurate for alkyl radicals. A comparison of benzene and naphthalene derivatives indicates that the heats of the links C–C and C–H are about 9 units higher when the carbon forms part of an aromatic ring, but as the basis of these calculations is somewhat doubtful, the aromatic compounds are omitted from the table. This uncertainty as to the effect on the C–H link of the state of combination of the carbon affects the values

[70] *Ber.*, 1920, **53**, 643; 1922, **55**, 2826.
[71] *Ber.*, 1919, **52**, 1501; 1920, **53**, 1347, 1519; 1923, **56**, 463.
[72] *Annalen*, 1924, **440**, 111.
[73] *Z. physikal. Chem.*, 1922, **102**, 134; *Z. Elektrochem.*, 1925, **31**, 474.
[74] Geiger–Scheel, "Handbuch der Physik," 1926, **24**, 532.
[75] "Handbuch der chemischen Physik," Leipzig, Akad. Verlagsges., 1930, p. 882.

given for multiple links of carbon to carbon, nitrogen, and other elements; these are calculated on the value found for C–H in the paraffins, as we have no means of finding its true value in the ethylene and acetylene derivatives. As they stand, the values for multiple links are interesting :

	Abs.	Rel.		Abs.	Rel.		Abs.	Rel.		Abs.	Rel.
C—C	71·0	1	C—N	55	1	C—O	70·5	1	C—S	58·7	1
C=C	125·2	1·8	C=N	111	2·0	C=O	163	2·3	C=S	127	2·2
C≡C	165	2·3	—C≡N	183	3·4	C≡O	235·5	3·3			
			—N≡C	184	3·4						

It is remarkable that while with the link of carbon to carbon the heat of formation increases much less rapidly than the number of links, which entirely agrees with what we should expect from the behaviour of unsaturated compounds, with the link of carbon to nitrogen, oxygen, or sulphur the heat of formation of a double link is at least twice, and that of a triple link more than three times, that of a single link.

As will be realised, the question of the heats of formation of links is of great importance, but so far the subject is little developed. We need to accumulate accurate data on the heats of atomisation of more of the elements, and the heats of combustion of a large number of compounds of the most varied types.

Dipole Moments.[76]

The methods of measurement described above give us the dipole moment of the whole molecule. This may be conceived to be made up of a series of partial moments pertaining to each of the links; these are obviously directed magnitudes, and their vector sum is the moment of the molecule. If we knew the values of each of the partial moments, and the angles which they make with one another, we could calculate the molecular moment. We cannot yet do this with any great accuracy, but it can often be done sufficiently nearly to enable us to decide between two chemically possible structures, and in this way the study of dipole moments has already proved of great value.

In the first place, if the molecule is non-polar, the partial moments must balance one another, and the molecule must be symmetrical. The diatomic elementary gases H_2, N_2, O_2, Cl_2, etc., are found to be non-polar, as we should expect. Triatomic molecules of the type AB_2 should be non-polar if the three atoms lie in a straight line,

[76] Complete lists of dipole moments published up to date will be found in Smyth, *op. cit.* (1931): also in Debye, " Polare Molekeln," Leipzig, Hirtzel, 1929, with supplementary lists for 1929 and 1930. Moments quoted without authority in the text (which are expressed in terms of the unit 1×10^{-18} E.S.U.) will be found in these lists.

provided the links are the same, as they usually will be; if the valencies are inclined to one another, the molecule will be polar. It has thus been shown that CO_2, CS_2, and N_2O are rectilinear, while H_2O, H_2S, and SO_2 are triangular. (Many of these conclusions are confirmed by the spectra, and also by the scattering methods of Debye and Wierl.) A molecule AB_3 will be non-polar if all the atoms lie in a plane and the valency angles are equal; hence NH_3, since it has a moment of 1·5, cannot be plane but must be pyramidal, as must PH_3 (0·55) and AsH_3 (0·15). A pentatomic molecule AB_4 can be non-polar on the tetrahedral model, or if the five atoms lie in a plane. CH_4 and CCl_4 are non-polar, and the plane formula is ruled out, because if it were true CH_2Cl_2 (in the *trans*-form, which must be the more stable) would be non-polar, whereas it has a moment of 1·5. Thus the tetrahedral configuration is established, and the square pyramid, which was at one time suggested, is shown to be impossible.

When we come to more complicated molecules, we need to get some idea of the moments of individual links. We have first, however, to find the direction or sense of the moments. This can be done by an ingenious method suggested by J. J. Thomson [77] and first used by J. W. Williams.[78] Since the benzene ring is planar, the moments of the links C–X, C–Y in a para-substituted molecule C_6H_4XY will lie in the same straight line. Hence if the direction of these moments with respect to the ring is the same, they will oppose, and if it is the opposite they will strengthen, one another. This enables us to divide the links into two classes of opposite sense : it is found, for example, that C–Cl, C–Br, and C–NO_2 belong to one class, and C–CH_3 and C–NH_2 to the other; and it is easy to see, on more general grounds, that the first class must have the negative end of the dipole remote from the ring.

In finding the moments of individual links, the first difficulty is that of the C–H link. All saturated paraffins (22 have so far been examined [79]) are non-polar; but it can easily be shown that, if we assume the tetrahedral model, this absence of polarity can be explained by the symmetry of the molecule, and is compatible with any value of the moment of C–H. There is good reason to think that this moment is small : it is commonly assumed to be 0·4 (Williams, and A. Eucken and L. Meyer [80]), but all that we really know is that it lies somewhere between 0·4 and zero. L. E. Sutton [81] has calculated the values for C–H and C–Cl from the observed

[77] *Phil. Mag.*, 1923, **46**, 513. [78] *Physikal. Z.*, 1928, **29**, 174.
[79] See R. W. Dornte and C. P. Smyth, *J. Amer. Chem. Soc.*, 1930, **52**, 3546.
[80] *Physikal. Z.*, 1929, **30**, 397.
[81] *Proc. Roy. Soc.*, 1931, **133**, 689, note.

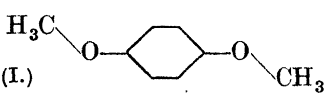
moments of chloroform and methylene chloride, using the angles between the C–Cl valencies given by the measurements of Debye and Wierl, on the assumptions (*a*) that the C–H valencies in methylene chloride have an angle of 109·5°, (*b*) that this angle is reduced by the expansion of the C–Cl angle to 100°. He finds that m(C–H) (this is a convenient symbol for the moment of the link C–H) is for (*a*) 0·15, and for (*b*) 0·20 : the corresponding values for m(C–Cl) are (*a*) 1·5 and (*b*) 1·41. The moment of C–H is in any case small, compared with most of those with which we have to deal, and we may provisionally assume the value 0·4. The moments of other links can then be calculated from the observed moments of the simpler molecules. For example, m(CH_3Cl) = 1·9 : the resultant of the moments of the three C–H links is equal (assuming angles of 109·5°) to that of one : hence m(H_3C–Cl) = m(H–C–Cl) = 1·9. As m(C–H) = 0·4, m(C–Cl) = 1·5. The uncertainty as to the value of m(C–H) implies that m(C–Cl) may be as large as 1·9. The moments of other links can be calculated by similar methods, and the results are given in Table III (p. 402), the atom which is at the positive end of the dipole being always printed first. These values are only provisional; they depend on three assumptions which cannot be strictly true : (1) the value for m(C–H); (2) the assumption that the value for a given link is unaffected by the other links in the same molecule : this seems to be approximately true except in the aromatic derivatives (see p. 392); (3) the assumption that the valency angles can be taken to be 109·5°. This last point involves two questions. As we saw from the distances in the chlorinated methanes, the angles between the valencies of a 4-covalent atom such as carbon vary to some extent with the nature of the atoms attached to it, but amounts of variation such as were found in these compounds would not change the values for the links by more than a few tenths of a unit. It is, however, maintained by Pauling[3] that with covalencies of 2 or 3 the normal angle is not 109·5° but 90°. This would make a more serious difference to the values calculated for the individual links, when the central atom has a covalency of less than 4. For example, water has a moment of 1·87. If the angle between the O–H valencies is 109·5°, m(O–H) = 1·87 ÷ 1·155 = 1·62. If it is 90°, m(O–H) = 1·87 ÷ 1·414 = 1·32. In the same way, m(NH_3) = 1·5; if the angles are tetrahedral, m(N–H) = 1·5 : if they are 90°, m(N–H) = 1·06. The figures in the table are calculated for angles of 109·5° and a C–H value of 0·4.

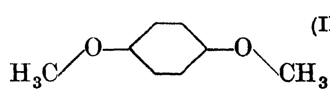
Inspection of the table shows that (1) the element of the earlier periodic group (counting hydrogen as belonging to Group I) is always positive so far as is known; but we do not yet know the moments of any links of carbon to elements in the first three groups other than

hydrogen. (2) In the link X–Y, where X and Y are in different periodic groups, if X, the positive member, remains the same, and Y represents a series of elements from the same group, the moment always diminishes as the atomic number of Y increases, except in C–O and C–F, which seem to have smaller moments than C–S and C–Cl; the exception does not hold with H–O and H–S: m(H–F) is of course unknown. On the other hand, if we keep Y (the negative member) constant, and replace X by another atom of the same periodic group, we get, so far as we can judge from the scanty data, the opposite result: the heavier X is, the larger the moment.

It will also be noticed that in the series H–C, H–N, H–O, though the increase is continuous, it is much greater between H–C (0·4) and H–N (1·5) than between H–N and H–O (1·6). This may be connected with the fact that in H–C alone the negative atom has no unshared valency electrons.

Flexible Molecules.—A conclusion of very general interest which emerges from the dipole measurements concerns the behaviour of "flexible" molecules and the meaning of the free rotation of singly linked atoms. As we have seen, a para-disubstituted benzene with the two substituents the same would be expected to have zero moment, and many such molecules, for example, p-$C_6H_4Cl_2$, p-$C_6H_4I_2$, p-$C_6H_4(CH_3)_2$, are found to be non-polar. But others are definitely polar: p-$C_6H_4(O{\cdot}CH_3)_2$ 1·74, p-$C_6H_4(CHO)_2$ 2·35, p-$C_6H_4(CH_2Cl)_2$, 2·23, etc. In all these it will be noticed that the resultant moment of the substituent group does not lie in the central line of the molecule; quinol dimethyl ether, for example, may, without any departure of the valency angles from the normal, have any configuration between (I) and (II).

(I.)


(II.)


Of these, (I) is symmetrical and non-polar, while (II) should have a considerable moment. The mutual repulsion of the dipoles would tend to make the molecules assume the non-polar form. L. Meyer [82] has pointed out that such molecules are under two opposing influences: (1) the work required to deflect the groups from the favoured position, which is the intramolecular potential of the dipoles, and (2) the energy of the thermal agitation, which is given by kT, where k is the gas constant per molecule ($= R/N$), and T the absolute temperature. If the potential is much the larger, the molecule will remain in its position of minimum (if it is symmetrical, of zero) moment; if the thermal energy is much the larger, the

[82] *Z. physikal. Chem.*, 1930, [*B*], **8**, 27.

potential will have a negligible effect, and the molecule will assume all possible positions with equal frequency. Meyer also shows [83] that the potential of the moments μ_1, μ_2, at a distance d apart is approximately $\mu_1 \cdot \mu_2/d^3$. Hence for a molecule at the ordinary temperature with two moments of the order of 1×10^{-18} E.S.U., the thermal energy $kT(4 \times 10^{-14}$ erg) will equal the potential if $d = 3 \times 10^{-8}$ cm., which is about twice the distance between two linked atoms (other than hydrogen) in an organic molecule. We should therefore expect that in a molecule such as ethylene dichloride the repulsion of the dipoles would have a large effect, while in quinol dimethyl ether and other *p*-di-substitution products of benzene, where the two dipoles are about 6 Å.U. apart, its effect would be very small. In compounds of the latter type, as we have seen, this is borne out by experiment; and with ethylene dichloride direct measurement with *X*-rays has shown [24] that the two C–Cl links are mainly in the most remote (" trans ") position, but that they are disturbed by thermal agitation to an extent which corresponds closely to that required to account for the observed dipole moment. With molecules of this type, for which the electrical and thermal energies are of comparable magnitude, it should be possible to show that the moment increases with rise of temperature. This has been the subject of a number of papers [84]; the facts are not yet quite certain, but seem on the whole to support the theory.

Chemists have long realised that the principle of free rotation of singly linked atoms with their attached groups did not necessarily imply that these atoms were continuously rotating; it was founded on the absence of isomerides capable of passing into one another by such rotation, and hence it only implied that the molecule was free to take up the most favoured of all the forms which this rotation permitted. The application of the methods of scattering, and of the measurement of dipole moments, has shown us how far and under what conditions the rotation can occur. It is clear that in considering, especially in relation to its reactivity, the forms which a complicated molecule can assume, we must take into account the effect of the forces between the dipoles on its configuration, and we are beginning to learn how this can be done.

The Co-ordinate Link.—The theory that a co-ordinate link is a covalency formed of two shared electrons, both derived from one of the two linked atoms, has been regarded by some chemists as

[83] For a further discussion of this, see C. P. Smyth, R. W. Dornte, and E. B. Wilson, jun., *J. Amer. Chem. Soc.*, 1931, **53**, 4242.

[84] L. Meyer, *loc. cit.*; R. Sänger, *Physikal. Z.*, 1931, **32**, 21; Meyer, *ibid.*, p. 260; Smyth and co-workers, *J. Amer. Chem. Soc.*, 1931, **53**, 527, 2005, 2988, 4242.

improbable, on account of the large electrostatic displacement which it implies; but the measurement of the moments of molecules containing such links has confirmed it. With the bivalent carbon compounds, such as carbon monoxide and the *iso*cyanides, there is evidence of the presence of a co-ordinate link in which the carbon acts as acceptor, and it has been shown [85] that the moments of these compounds agree closely with those to be expected if an electron is transferred from the nitrogen or oxygen to the carbon. Again, a series of co-ordinated compounds have been shown to have exceptionally large moments (from 4 to 9 units), such as the sulphoxides and sulphones,[86] and the compounds of the halides of beryllium, boron, and aluminium with ethers, nitriles, and amines.[87] The abnormal increase of molecular polarisation with concentration shown by the alcohols [88] indicates that their association is accompanied by the formation of co-ordinate links of large moment. The relation between the power of a hydrogen atom to act as acceptor, and the position in the periodic table of the atom to which it is already attached, again supports the theory.[89] It is well known that this power varies greatly : the hydrogen in C–H cannot act as acceptor : in N–H it does so reluctantly, in O–H and F–H very readily. In the same way the co-ordinating power of the hydrogen is much greater in N–H than in P–H, in O–H than in S–H, and in F–H than in Cl–H; its power in X–H increases as X changes from an earlier to a later group in the first period, or within a given group from the second period to the first. But these are precisely the directions in which the moment of X–H, in which H is always positive, increases; and if the formation of a co-ordinate link consists in the hydrogen taking a share in a pair of unshared electrons of another atom, we should expect it to do so the more readily, the larger its positive charge.

Dipole Moment and Organic Structures.

The study of dipole moments has thrown light on a whole series of problems of structure in organic chemistry, and the results may be briefly summarised.

(1) *Substitution in Benzene.*—The theories of the influence of groups on the reactivity of organic molecules which have been put

[85] D. L. Hammick, R. C. A. New, N. V. Sidgwick, and L. E. Sutton, *J.*, 1930, 1876.

[86] E. Bergmann, L. Engel, and S. Sándor, *Z. physikal. Chem.*, 1930, [*B*], **10**, 397; O. de Vries and W. H. Rodebush, *J. Amer. Chem. Soc.*, 1931, **53**, 2888.

[87] H. Ulich and W. Nespital, *Z. angew. Chem.*, 1931, **44**, 750.

[88] L. Lange, *Z. Physik*, 1925, **33**, 169; J. Errera, Leipziger Vorträge, 1929, pp. 25, 105.

[89] N. V. Sidgwick, *Z. Elektrochem.*, 1928, **34**, 449.

forward by Lapworth, Robinson, Ingold, and others agree in ascribing the phenomena to a displacement of the electrons in the molecule, and any such displacement must be reflected in the dipole moments. The first attempt to test these theories from the physical side has been made by L. E. Sutton,[90] with respect to the problem of substitution in benzene. The moment of a molecule R–X is different according as R is an alkyl or an aryl group; and Sutton has shown that there is a simple relation between the sign of this difference and the directing power of the group X in benzene. If we call those moments of which the positive end is away from R positive, and those in the opposite direction negative, then if m(Ar–X) – m(Alk–X) is positive, X directs ortho-para: if it is negative, X directs meta. For example:

m(Ar–CH_3)	+ 0·45	:	m(Alk–CH_3)	0	:	Diff.	+ 0·45
m(Ar–NH_2)	+ 1·55	:	m(Alk–NH_2)	+ 1·23	:	Diff.	+ 0·32
m(Ar–Cl)	– 1·56	:	m(Alk–Cl)	– 2·15	:	Diff.	+ 0·59
m(Ar–CCl_3)	– 2·07	:	m(CH_3·CCl_3)	– 1·57	:	Diff.	– 0·50
m(Ar–NO_2)	– 3·93	:	m(Alk–NO_2)	– 3·05	:	Diff.	– 0·88

The first three groups of course direct ortho-para, the last two meta. Wherever this rule has been tested it has been found to hold.

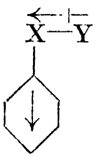
These results strongly support the view that the electrons of the benzene ring are liable to suffer displacement under the influence of a substituent, and that this determines the position which further substituents take up; moreover the direction of the displacement is that postulated for the electromeric effect by the Lapworth–Robinson theory. The observed displacement, as the above examples show, is of the order of one-tenth of that which would be caused by the transference of an electron from one atom of the ring to the next (about 7·4 units), and we might suppose either that a small proportion of the molecules underwent the full transference, or that all of them suffered a small displacement. As Sutton points out, the latter must be true, since in chlorobenzene, for example, substitution is much slower than in benzene; if only a small proportion of the molecules were affected, the rest would react as easily as before, and the rate of reaction of the compound as a whole would not be seriously diminished.

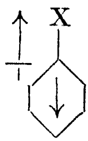
It is of interest to compare this conclusion of Sutton's with the substitution rule put forward by D. L. Hammick and W. S. Illingworth.[91] This rule, which seems to hold in every case, states that if in C_6H_5–X–Y, Y is in a later periodic group than X, then the direction is meta, but that if not (*i.e.*, if it is in the same or an earlier group, or if there is no Y, as in C_6H_5Cl) then it is ortho-para. Now

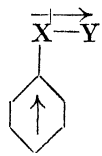
[90] *Proc. Roy. Soc.*, 1931, **133**, 668.

[91] *J.*, 1930, 2358.

in a link X−Y, as we have seen, if Y belongs to a later periodic group than X, it is the negative end of the dipole, but if to an earlier, the positive end. If we accept the conclusion, that the ortho-para directing power involves an electronic drift in the ring away from the substituent, we can distinguish three cases (the arrow in the ring indicates the drift) :

(I.) 
o, p.

 (II.)
o, p.

 (III.)
m.

In the first and third, the drift is in the same direction as the moment of the substituent, and may be supposed to tend to relieve the strain which this causes; but in the second, where there is only one atom in the substituent group, we have to assume a drift in the opposite direction to the moment, which indicates that some principle, other than induction, is operative, which we do not understand.

(2) *Diphenyl Derivatives.*—The Kaufler formula for diphenyl, in which one ring was supposed to be folded over on the other,[92] was disproved by dipole measurements,[93] which showed that the *p,p'*-di-derivatives $X{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}X$ had almost the same moments as the corresponding *p*-di-derivatives of benzene; they were non-polar so long as the moment of X was symmetrical to the central axis of the molecule, and only polar when this could be explained by the flexibility of the X group.

(3) cis - trans - *Isomerism.* — A *cis* - disubstituted ethylene, CHX:CHX, should be polar, and its *trans*-isomeride non-polar, so that the moments give a simple method of determining the configuration. This test has been applied by J. Errera [94] to the dihalogen substitution products of ethylene. He finds that the dichloride, dibromide, and chlorobromide in the *trans*-form are

[92] For a summary of the chemical arguments for and against this formula, see C. K. Ingold, *Ann. Reports*, 1926, **23**, 119. For the explanation of the optical activity of diphenyl derivatives, see F. Bell and J. Kenyon, *Chem. and Ind.*, 1926, **4**, 864; W. H. Mills, *ibid.*, p. 884; W. H. Mills and K. A. C. Elliott, *J.*, 1928, 1291.

[93] J. W. Williams and A. Weissberger, *J. Amer. Chem. Soc.*, 1928, **50**, 2332; *Z. physikal. Chem.*, 1929, [*B*], **3**, 367; A. Weissberger and R. Sängewald, *ibid.*, [*B*], **5**, 237; J. W. Williams and J. M. Fogelberg, *Physikal. Z.*, 1930, **31**, 363.

[94] *Compt. rend.*, 1926, **182**, 1623; *Physikal. Z.*, 1926, **27**, 764; "Polarisation diélectrique," Paris, 1928.

non-polar, and in the *cis*-form have moments of about 1·5: with the chloroiodides one form has $\mu = 0{\cdot}57$ and the other $\mu = 1{\cdot}27$. Since the moments of C–Cl and C–Br are practically identical, while that of C–I is smaller, we should expect a residual moment in the *trans*-chloroiodide but not in the *trans*-chlorobromide. The assignment of structures previously made to the isomerides on other grounds agrees with the dipole measurements, except in the chloroiodides.

This conclusion has been confirmed for the dichlorides by Debye,[24] who has shown by the *X*-ray method that the distance between the chlorine atoms in the *cis*-compound is 3·6 and in the *trans*-compound 4·7 Å.U.

(4) *Compounds of Type* CA_4.—The configuration of these compounds has been the subject of much discussion. Guillemin and V. Henri suggested, on the basis of spectroscopic measurements,[95] that a molecule CA_4 could have the form of a square pyramid with the carbon at the apex. The *X*-ray examination of the crystal structure of pentaerythritol, $C(CH_2{\cdot}OH)_4$, was believed to indicate that the arrangement of the groups round the central carbon atom could not be tetrahedral.[96] Later work has weakened the force of both of these lines of argument.[97] The dipole moments appear to be conclusive in favour of the tetrahedral structure. CH_4, CCl_4, $C(NO_2)_4$, and $C(CH_2hal)_4$, where hal = Cl, Br, I, have all been shown to be non-polar. On the other hand, compounds CA_4 in which A = $O{\cdot}CH_3$, $O{\cdot}C_2H_5$, $CH_2{\cdot}OH$, $CH_2{\cdot}O{\cdot}CO{\cdot}CH_3$, $CH_2{\cdot}O{\cdot}NO_2$, $CO{\cdot}O{\cdot}CH_3$, $CO{\cdot}O{\cdot}C_2H_5$ have moments from 0·8 to 3·9.[98] These, however, are all groups with unsymmetrical moments, whose flexibility is sufficient to account for their polarity. The absence of polarity in pentaerythritol tetrachloride, tetrabromide, and tetraiodide, which was confirmed for the first two by the beam method, is remarkable. A symmetrical and non-polar arrangement of the four CH_2hal groups is of course possible, but it seems unlikely that the potential of the moments would be sufficient to fix the

[95] V. Guillemin, *Ann. Physik*, 1926, **81**, 173; V. Henri, *Chem. Reviews*, 1927, **4**, 189.

[96] H. Mark and K. Weissenberg, *Z. Physik*, 1923, **17**, 301; M. L. Huggins and S. B. Hendricks, *J. Amer. Chem. Soc.*, 1926, **48**, 164.

[97] For the spectroscopic evidence, see A. E. Ruark and H. C. Urey, "Atoms, Molecules, and Quanta," 1930, p. 436; for the crystal structure, I. Nitta, *Bull. Chem. Soc. Japan*, 1927, **1**, 62; A. Schleede, *Z. anorg. Chem.*, 1928, **168**, 313; **172**, 121; also H. Möller and A. Reis, *Z. Krist.*, 1928, **68**, 385; (Miss) I. E. Knaggs, *Proc. Roy. Soc.*, 1929, **122**, 69.

[98] J. W. Williams, *Physikal. Z.*, 1928, **29**, 683; L. Ebert, R. Eisenschitz, and H. von Hartel, *Z. physikal. Chem.*, 1928, [*B*], **1**, 94; I. Estermann, *ibid.*, 1929, [*B*], **2**, 287; Leipziger Vorträge, 1929, p. 17; O. Fuchs, *Z. Physik*, 1930, **63**, 824.

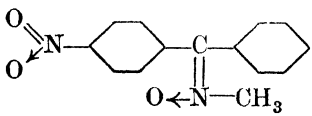
molecules in this position, especially as the orthocarbonates, $C(Oalk)_4$, are polar. It is probable that steric influences co-operate.[99]

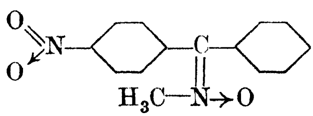
(5) *Bivalent Carbon Compounds.*—The dipole moments indicate that in carbon monoxide and the *iso*cyanides the carbon is triply linked to the oxygen or the nitrogen, the third link being co-ordinate :

$$O \equiv C \qquad\qquad R—N \equiv C$$

The link of carbon to oxygen or nitrogen has, as we have seen, a considerable moment, the carbon being positive. $C=O$ and $R—N=C$ should therefore be highly polar, and the moment in the latter should have its positive end remote from the group R. Carbon monoxide is almost non-polar (0·1), and it has been shown [85] that the moment of the $^{-}$NC group in the aryl *iso*cyanides (3·5) is in the opposite direction. This can only be explained by the transference of an electron to the carbon in the formation of the (third) co-ordinate link, and the effect of such a transference through the distance separating the two atoms is in good agreement with the magnitudes of the observed moments. The existence of a triple link between the atoms is confirmed by the heats of formation and the parachors, and further for carbon monoxide by the interatomic distance (obs. 1·14, calc. 1·13 Å.U.) and by the force constant ($18·6 \times 10^5$).

(6) *Oximes.*—A decision between the opposed theories of Hantzsch and Meisenheimer as to the configuration of the *syn-* and *anti-*oximes has been promoted by the measurement of the moments of

(I.) 

 (II.)

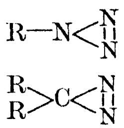
the *N*-ethers of *p*-nitrobenzophenoneoxime.[100] The $-N \longrightarrow O$ group should have a moment comparable with that of the nitro-group, and hence the moment of the *syn*-compound (I) should be large, and that of the *anti*-compound (II) small. It was found that the α-compound (m. p. 159°), which according to Meisenheimer has the *syn*-formula, gave $\mu = 6·60$, and the β-compound (m. p. 136°), 1·09. This seems conclusive in favour of the Meisenheimer theory. The only known *N*-ether of *p*-nitrobenzaldoxime was found to have a moment of 6·4, indicating the *syn*-configuration.

(7) *Azo-compounds.*—It was pointed out long ago by Hantzsch that the remarkable stability of azobenzene (b. p. 293°) shows that it must have the more stable *anti*-configuration. This has been confirmed by the dipole moment, which is zero. The *p*-monochloro-

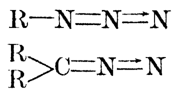
[99] A. Weissberger and R. Sängewald, *Physikal. Z.*, 1929, **30**, 792.
[100] L. E. Sutton and T. W. J. Taylor, *J.*, 1931, 2190.

and *p*-monobromo-derivatives have almost the same moments [101] (1·55 and 1·42) as chloro- and bromo-benzene (1·55 and 1·52).

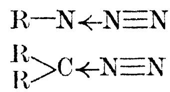
(8) *Azides and Aliphatic Diazo-compounds.*—These compounds were originally assumed to have ring structures, but this view was later abandoned in favour of open-chain formulæ, mainly through the work of Thiele and Staudinger, who showed that they gave derivatives containing these open chains. This argument is not conclusive, because the double link between nitrogen atoms (unlike that between carbons) is very strong, and the rings, if present, are more likely to break at the single link. The possible structures, assuming that the atoms have complete octets, are



(I.)



(II.)



(III.)

Of these, formula (I) should have a small moment, owing to the symmetry of the ring, while the moments of (II) and (III) should be large, because they contain a co-ordinate link. The volatility of the azides and diazo-compounds suggests [102] that they have small moments; the parachor values [103] are also in favour of the ring structures, though the difference between the two calculated values is so small that this cannot be regarded as decisive. Recently, the moments of phenyl-, *p*-tolyl-, and *p*-chlorophenyl-azides have been found [104] to be 1·55, 1·96 and 0·35, indicating that the N_3 group has a moment of about 1·5, with the negative end away from the aromatic ring. This is the wrong direction for structure (III), and too small for (II), which should have a moment of 3—4 (compare diphenyl sulphoxide, $R_2S \longrightarrow O$, $\mu = 4{\cdot}1$). Also the practical absence of polarity in the *p*-chloro-compound indicates that the moment of the group is symmetrical to the axis, and this is possible only for structure (I).

Thus the moments favour the ring structure for the aromatic azides. This is remarkable, since the *X*-ray examination of the crystal structure of the metallic azides has shown [105] that the azide ion has a rectilinear configuration. This implies the presence of two double links, so that the ion must be written $N \overset{\leftarrow}{=} N \overset{\rightarrow}{=} N$ or $\overset{-}{N}=\overset{+}{N}=\overset{-}{N}$; it is thus quite symmetrical, and has no turning

[101] E. Bergmann, L. Engel, and S. Sándor, *Ber.*, 1930, **63**, 2572.

[102] N. V. Sidgwick, *J.*, 1929, 1108.

[103] H. Lindemann and H. Thiele, *Ber.*, 1928, **61**, 1529.

[104] L. E. Sutton, *Nature*, 1931, **128**, 638; E. Bergmann and W. Schutz, *ibid.*, p. 1077.

[105] S. B. Hendricks and L. Pauling, *J. Amer. Chem. Soc.*, 1925, **47**, 2904.

moment; but if it passes into the covalent state by the addition of an imaginary phenyl kation, this must attach itself to a terminal nitrogen, giving the highly polar and so presumably less stable structure (II). This may be why the ion and the covalent form have different structures.

The moments of the aliphatic diazo-compounds have not yet been determined. Preliminary (unpublished) measurements by L. E. Sutton indicate that they are not large, as the volatility also suggests, and so favour the ring structures. The supposed optical activity found in the diazo-compounds by P. A. Levene, W. A. Noyes, and H. Lindemann, which would necessitate structure (III), has been shown to be due to an impurity.[106]

General Stereochemical Conclusions.

The classical methods of stereochemistry have shown that there is a tetrahedral arrangement of the groups surrounding 4-covalent atoms of beryllium, boron, carbon, nitrogen, silicon, phosphorus, sulphur, copper, zinc, arsenic, selenium, tin, and tellurium [107]; and an octahedral round 6-covalent atoms of aluminium, chromium, iron, cobalt, nickel,[108] copper, arsenic, rhodium, iridium, and platinum. The examination of crystal structures shows that these configurations, for 4- and 6-covalent atoms respectively, are almost universal. The only exceptions for which there is experimental evidence are the 4-covalent compounds of bivalent palladium and platinum, and quite recently, nickel. Werner's view that the 4-covalent platinous compounds have the four groups and the central atom in a plane was attacked by Reihlen,[109] but has apparently been vindicated by A. Hantzsch,[110] who showed that the two forms of $Pt(py)_2Cl_2$ have the same molecular weight in phenol. With palladium, F. Krauss and F. Brodkorb [111] obtained isomeric forms of the analogous $Pd(py)_2Cl_2$ and of $Pd(C_2H_5{\cdot}NH_2)_2Cl_2$, and showed that these had the same simple molecular weight in solution. T. M. Lowry [112] adduced evidence of a different kind in favour of these plane structures. He pointed out that R. G. Dickinson [113] had found that while zinc, cadmium, and mercuric salts of the type $K_2[X(CN)_4]$ formed cubic crystals, whose structure indicated a tetrahedral form of the ion, the salts $K_2[PdCl_4]$, $(NH_4)_2[PdCl_4]$, and

[106] A. Weissberger and R. Haase, *Ber.*, 1931, **64**, 2896.

[107] For tellurium, see H. D. K. Drew, *J.*, 1929, 560; T. M. Lowry and F. L. Gilbert, *ibid.*, p. 2867.

[108] G. T. Morgan and F. H. Burstall, *Nature*, 1931, **127**, 854; *J.*, 1931, 2213.

[109] H. Reihlen and K. T. Nestle, *Annalen*, 1926, **447**, 211.

[110] *Ber.*, 1926, **59**, 2761.

[111] *Z. anorg. Chem.*, 1927, **165**, 73.

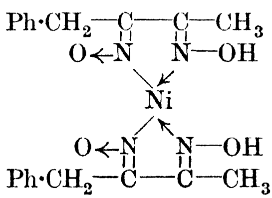
[112] *Nature*, 1929, **123**, 548.

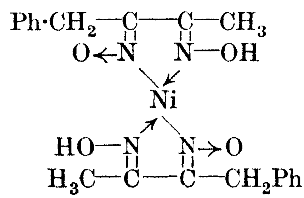
[113] *J. Amer. Chem. Soc.*, 1922, **44**, 774, 2404.

$K_2[PtCl_4]$ formed tetragonal crystals, in which X-ray analysis showed the metal to be at the centre of a square, with the chlorine atoms at the four corners.

On the other hand, F. G. Angell, H. D. K. Drew, and W. Wardlaw [114] have examined the two forms of the thioether compound $(Et_2S)_2PtCl_2$, and find that, while both have the normal molecular weight in benzene, their chemical behaviour shows greater differences than *cis-trans* isomerism will account for. In particular, with silver oxide the α-form reacts slowly with liberation of the thioether and precipitation of platinous oxide or hydroxide, while the β-form is rapidly converted into the soluble and fairly strong base $(Et_2S)_2Pt(OH)_2$. The structures which they propose for the two forms seem for various reasons unsatisfactory, but their results certainly indicate that these compounds need further investigation.

This question assumes peculiar interest in the light of Pauling's recent conclusion from wave mechanics [3] that bivalent nickel, palladium and platinum, unlike the non-transitional elements, can form 4-covalent compounds of the plane type, which can further be distinguished by their smaller paramagnetic moments. This conclusion has recently been supported by the discovery of S. Sugden [115] that the nickel compound of benzylmethylglyoxime occurs in two isomeric forms





and that these are diamagnetic. With a tetrahedral configuration the two forms would be optical antimerides, and should be paramagnetic.

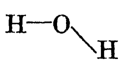
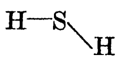
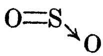
The general principles of structure which these physical investigations show to be applicable to the volatile compounds of the lighter elements, with which we are mainly concerned, may be briefly summarised. G. N. Lewis's conception of the two-electron link, in which the electrons may come either one from each of the linked atoms (normal) or both from one (co-ordinate), holds for all but a few molecules,[3] and the dipole moments indicate that the electrons are shared nearly (within 20%) equally between the two atoms. The maintenance of the valency octet is a condition of stability which is almost always fulfilled. For the configuration of the molecules the tetrahedral atomic model of van 't Hoff has received

[114] *J.*, 1930, 349. [115] *J.*, 1932, 246.

the fullest support, not only for atoms forming four, but also for those forming two or three links, although in the two last cases Pauling's theoretical conclusions indicate a valency angle of 90° rather than 109·5°, a view which it is not yet possible to test experimentally. The valency angles can change to some extent with the nature of the groups in the molecule, but apparently not much more than 15%.

The effective radii of the atoms are now known, and are evidently remarkably constant factors in determining the configuration of the molecule; apart from certain ascertained changes due to the multiplicity of the link (up to 20%) and in crystals to the nature of the lattice (rarely more than 5%), the differences between observed and calculated values of the distances between linked atoms scarcely exceed the experimental error. But the form which the molecule assumes, through the liberty of free rotation of singly linked atoms, without change of the valency angles or of the length of the links, is largely determined by the intramolecular attractions of its dipoles, especially when these are near together.

As a final example, we may repeat the conclusions reached for a series of familiar triatomic molecules :

		Rectilinear.
O=C=O, S=C=S	:	Spectrum, dipole moment.
$[N\overset{\leftarrow}{=}N\overset{\rightarrow}{=}N]^-$	:	Crystal structure.
$N\overset{\leftarrow}{=}O\overset{\rightarrow}{=}N$	:	Spectrum, dipole moment.
$[C=N=O]^-$	:	Crystal structure.
H—C≡N	:	Spectrum.
		Triangular.
	:	Spectrum, dipole moment.
	:	Dipole moment.
	:	Spectrum, dipole moment.

The last example may be dealt with in more detail. The alternative structure O=S=O gives the sulphur a valency group of 10 electrons, 8 being shared. This would presumably imply a straight line molecule, but we cannot be sure what effect the decet would have. It is, however, a very improbable structure, because a valency group of more than 8 electrons never occurs unless either (*a*) they are all shared or (*b*) it can be reduced to the normal form by assuming that two of the electrons become inert; but (*b*) is only found in the heavier elements. The chemistry of sulphur supports this conclusion. A quadrivalent and 4-covalent sulphur atom never occurs; the stability of the optically active compounds of the type $RR_1S{\rightarrow}O$

proves that they cannot assume the tautomeric form $RR_1S{=}O$ (containing the decet) which would lead to racemisation; while SCl_4 has been shown by T. M. Lowry and G. Jessop [115a] to occur only in the solid state, and then probably as the salt $[SCl_3]Cl$. The final proof that in SO_2 one of the oxygen atoms is singly and the other doubly linked is given by the values of the force constants for the two links, which are 7·23 and 4·93 × 10^5 respectively.

TABLE I.

Substance.	Link.	Interatomic distance. × 10^8 cm.	Refs.	Force constant *f*. × 10^{-5} dynes/cm.	Refs.	Mean restoring force of vibration, *K*. × 10^4 dynes.	Refs.	Dissociation energy, *A*. Kilocals./g.-molecule at const. pressure.	Refs.
H_2	H—H	0·749	123	5·06	128	4·55	15	103	116
O_2	O=O	1·205	124	11·3	128	4·14	15	118	117
N_2	N≡N	1·107	125	22·2	128	7·14	15	208	118
F_2	F—F	1·35	126					63·5	119
Cl_2	Cl—Cl	1·93	126	3·21	129	1·32	15	57·4	120, 121.
Br_2	Br—Br	2·26	127	2·47	121			45·8	121
I_2	I—I	2·66	126	1·69	121			36·0	122
HF	H—F	0·929	7					146·5	
HCl	H—Cl	1·282	7	4·4	130	3·47	15	102·2	
HBr	H—Br	1·421	7	3·56	131	2·94	15	86·7	
HI	H—I	1·617	7	2·9	131	2·52	15	70·9	
H_2O	H—O							110	
$CH_3{\cdot}OH$	H—O			6·34	132	4·59	15		
NH_3	H—N							89·8	
$CH_3{\cdot}NH_2$	H—N			6·04	132	4·45	15		
H_2S	H—S							87·4	
$CH_3{\cdot}SH$	H—S			3·77	133	3·09	15	83·3	
CH_4	H—C			4·58	134	3·62	15	93·6	
C_2H_6	C—C			4·31	135	2·05	15	71·0	
C_2H_4	C=C			9·36	135	3·88	15	125·2	
C_2H_2	C≡C			16·4	136	6·32	15	165	
$CH_3{\cdot}NH_2$	C—N			4·86	132	2·22	15	55	
$CH_3{\cdot}NCO$	C=N							111	
HCN	C≡N							180	
$CH_3{\cdot}CN$	—C≡N			17·9	137	6·17	15	188	
$CH_3{\cdot}NC$	—N≡C							184	
$CH_3{\cdot}OH$	C—O			4·99	132	2·25	15	70·5	
$(CH_3)_2O$	C—O							72·6	
CO_2	C=O							181·3	
H_2CO	C—O			11·9	137	4·49	15	160	
$(CH_3)_2CO$	C=O							165	
CO	C≡O	1·14	6	18·6	15	6·28	15	235·5	
$(CH_3)_2S$	C—S							58·7	
$CH_3{\cdot}SH$	C—S			3·01	133	1·44	15		
CS_2	C=S							127	
CH_3Cl	C—Cl			3·12	138	1·48	15	73·2	
CCl_4	C—Cl							72·5	
CH_3Br	C—Br			2·61	139	1·23	15	60·0	
CH_3I	C—I			2·15	139	1·05	15	42·8	
SO_2	S=O							126·9	

[115a] *J.*, 1930, 782.

Table II.

A. *Atomic Radii in Å.U.: from the Elements.*

Element.	Radius.	State.	Ref.	Element.	Radius.	State.	Ref.
H	0·37	Gas	123	Si	1·17	Solid	21
C	0·77	Diamond	60	Cu	1·28	Metal	146
N	0·55	Gas	125	Ag	1·44	Metal	146
O	0·60	Gas	124	Be	1·12	Metal	147
F	0·68	Gas	126	Zn	1·33	Metal	147
Cl	0·97	Gas	126	Cd	1·49	Metal	147
Br	1·13	Gas	127	Ge	1·22	Metal	21
I	1·33	Gas	126	Sn	1·40	Grey tin	21

B. *Dimensions of Links in Å.U.*

Compound.	Link.	Distance. Calc.	Distance. Corr.	Distance. Obs.	Ref.
HF	H—F	1·05		0·93	7
HCl	H—Cl	1·34		1·28	7
HBr	H—Br	1·50		1·42	7
HI	H—I	1·70		1·62	7
H_2O	H—O	0·97	1·08	1·03	140
NH_3	H—N	0·92	1·10	0·97	141
CO	C—O	1·37	1·13	1·14	6
N_2O	N—N	2·30	2·37	2·38	34, 142
CO_2	O—O	2·52		2·25	24, 27, 34
H_2S	H—S	1·41		1·25	143
CS_2	S—S	3·63	3·40	{3·05 {3·20	24 27, 34
H_2CO	C—O	1·37	1·15	1·2	144
$KClO_4$	Cl—O	1·56	1·67	1·56	153
K_2SO_4	S—O	1·64		1·66	58
H_3CCl	C—Cl	1·74		1·83	25, 26
CCl_4	C—Cl	1·74		1·85	25, 26
CBr_4	C—Br	1·90		2·05	34
$SiCl_4$	Si—Cl	2·14		2·02	34
$GeCl_4$	Ge—Cl	2·19		2·10	34
$SnCl_4$	Sn—Cl	2·37		2·33	34

Compound.	Link.	Distance. Calc.	Distance. Obs.	Ref.
CuCl	Cu—Cl	2·25	2·34	145
CuBr	Cu—Br	2·41	2·46	145
CuI	Cu—I	2·61	2·62	145
Cu_2O	Cu—O	1·88	1·85	58
Cu_2S	Cu—S	2·32	{2·42 {2·31	58 21
Ag[F]	Ag—F	2·12	2·46	58
Ag[Cl]	Ag—Cl	2·41	2·77	21
Ag[Br]	Ag—Br	2·57	2·88	21
Ag[I]α	Ag—I	2·77	3·05	21
AgIβ	Ag—I	2·77	2·81	21
Ag_2O	Ag—O	2·04	2·04	21
Ag_2S	Ag—S	2·48	2·61	58
BeO	Be—O	1·72	1·65	145
BeS	Be—S	2·16	2·10	21
ZnF_2	Zn—F	2·01	2·04	21
ZnO	Zn—O	1·93	1·97	21
ZnS	Zn—S	2·37	2·35	58
Cd[F]	Cd—F	2·17	2·34	21
Cd[O]	Cd—O	2·09	2·35	21
CdS	Cd—S	2·53	2·53	21

Table III.

Dipole Moments of Links, $\times 10^{18}$.

H—C 0·4	H—N 1·5	H—O 1·6	H—F (2)	
	H—P 0·55	H—S 0·8	H—Cl 1·03	
	H—As 0·15		H—Br 0·78	
			H—I 0·38	
	C—N 0·4	C—O 0·7	C—F 1·3	
		C=O 2·3		
	C≡N 3·1			
		C—S 1·0	C—Cl 1·5	
		C—Se 0·9	C—Br 1·4	
		C—Te 0·7	C—I 1·2	
P—Cl 0·8	As—Cl 2·0	Sb—Cl 3·8	P—Br 0·6	As—Br 1·7

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